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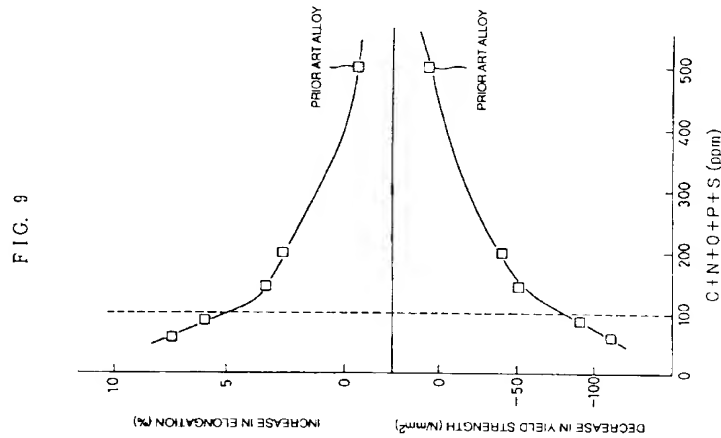
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(54) **Fe-Cr ALLOY EXCELLENT IN WORKABILITY.**

(57) An Fe-Cr alloy having an excellent workability over a wide range of the Cr content (e.g. 3-60 wt.%) by

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limiting the total content of C, N, O, P and S to 100 ppm or less. Fe-Cr alloys with various characteristics can be obtained by adding various combinations of the following element groups (1 to 4) to the Fe-Cr alloy of the basic composition: (1) a group consisting of Ni, Co and Cu with a total content of the elements in a specified range, contributing to an increase in acid resistance; (2) a group consisting of Al, Si and Mn and/or a group consisting of Ca, Mg and REM each with a total content of the elements in a specified range, contributing to an increase in oxidation resistance; (3) a group consisting of Ti, Nb, Zr, V, Ta, W and B with a total content of the elements in a specified range, contributing to an increase in high-temperature strength, and (4) a group consisting of Mo alone with a content thereof in a specified range, contributing to an increase in pitting resistance.



INDUSTRIAL UTILITY FIELD

The present invention relates to an Fe-Cr alloy having a significantly improved workability.

The present invention also relates to an Fe-Cr alloy having an improved workability as well as an
5 excellent acid resistance.

Furthermore, the present invention relates to an Fe-Cr alloy having an improved workability as well as an excellent oxidation resistance.

Still further, the present invention relates to an Fe-Cr alloy having an improved workability as well as excellent acid resistance and oxidation resistance.

BACKGROUND ART

Fe-Cr alloys are generally known to be materials of excellent corrosion resistance. Various improvements in the corrosion resistance, workability, and other physical properties have been proposed for such
15 Fe-Cr alloys including the following proposals.

Japanese Patent Publication No. 63-58904 proposes a ferritic stainless steel having a Cr content of from 11.0 to 16.0% by weight, wherein Ti is added to a predetermined amount. This material has excellent bulging properties as well as secondary workability.

Japanese Patent Publication No. 64-6264 proposes a bright annealed stainless steel plate having a Cr
20 content of from 8.0 to 35.0% by weight, wherein Si, Mn and Nb are respectively added to a predetermined amount. This material has an excellent rust resistance.

Japanese Patent Publication No. 2-1902 proposes an Fe-Cr alloy having a Cr content of more than 20.0% by weight and up to 25% by weight, wherein Mo, Mn and Nb are respectively added to a predetermined amount. This material is a ferritic stainless steel having an excellent high-temperature
25 cracking resistance upon welding as well as weld toughness.

Japanese Patent Application Kokai No. 61-186451 proposes an Fe-Cr alloy having a Cr content of from 25 to 50% by weight, wherein Si, Mn and Mo are respectively added to a predetermined amount. This material is an alloy having an excellent acid resistance.

Japanese Patent Application Kokai No. 62-267450 proposes an Fe-Cr based alloy having a Cr content
30 of from 16 to 19% by weight wherein Mo is added to a predetermined amount. This material is a high-purity ferritic stainless steel having an excellent intergranular corrosion resistance.

Japanese Patent Application Kokai No. 1-287253 proposes an Fe-Cr-Al alloy having a Cr content of 15 to 26% by weight and an Al content of from 4 to 6% by weight, wherein a rare earth element is added to a predetermined amount. This material is an Al-containing ferritic stainless steel having an excellent oxidation
35 resistance as well as production feasibility.

Japanese Patent Application Kokai No. 2-232344 proposes an Fe-Cr based alloy having a Cr content of from 25.0 to 30.0% by weight, wherein Mo is added to a predetermined amount. This material is a ferritic stainless steel having an excellent resistance to adhesion of organisms as well as a high resistance to sea
40 water corrosion.

Japanese Patent Application Kokai No. 3-2355 proposes an Fe-Cr alloy having a Cr content of from 16.0 to 25.0% by weight, wherein Nb is added to a predetermined amount determined in relation to the total content of C and N. This material is a ferritic stainless steel having excellent cold workability, toughness and corrosion resistance.

SUMMARY OF THE INVENTION

[A] Inventions of category A

The Fe-Cr alloys as described above contain a relatively large amount of Cr since corrosion resistance
50 was of prime importance in these alloys. As a result, these alloys occasionally suffered from poor ductility, and hence, insufficient workability. When such materials are used in such application as automobile exterior material or a building exterior material wherein the material should be press-worked, they suffer from such problems as cracking upon working, or an extreme difficulty in working due to strict working conditions. As set forth above, there is a strong demand for an improvement of such materials in their workability.

In view of the above-described situation, an object of the present invention is to provide an Fe-Cr alloy
55 which has an improved workability as well as sufficient acid resistance and oxidation resistance.

In order to achieve the above-described object, the inventors of the present invention have made an extensive study and surprisingly found that an Fe-Cr alloy wherein the contents of impurities including C, N,

O, P and S, which had been present in conventional Fe-Cr alloys, are reduced to an extremely low level would have a markedly superior ductility. The present invention is based on such a finding.

According to the present invention, there is provided a novel Fe-Cr alloy having an excellent workability characterized in that the alloy comprises 3 to 60% by weight of Cr; and 100 ppm or less in total content of C, N, O, P and S; the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and at least one member selected from Ni, Co and Cu at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (1);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability and oxidation resistance characterized in that the alloy comprises 3 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and at least one member selected from Si, Mn and Al at a content that meets the following relation (2):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (2),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (3);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, acid resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; at least one member selected from Ni, Co and Cu at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (1);$$

and at least one member selected from Si, Mn and Al at a content that meets the following relation (2):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (2),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (3);$$

the balance being Fe and inevitable impurities.

[B] Inventions of category B

The Fe-Cr alloys as described above contain a relatively large amount of Cr since corrosion resistance is of prime importance in these alloys. As a result, these alloys may occasionally suffer from poor ductility, and hence, insufficient workability to render working of the alloy material into the shape required by the specific application difficult, or in some cases, impossible. For example, when such materials are worked into a pipe and used in pipeworking after bending, the pipe often undergo such troubles as breaking upon bending. As set forth above, there is a strong demand for an improvement of such materials in their workability.

Furthermore, high-temperature strength of such materials is yet insufficient for such applications as automobile exhaust gas pipes wherein the material is exposed to a high temperature. Accordingly, there is also a demand for a further improvement in high-temperature strength and high-temperature fatigue properties. Still further, acid resistance of such materials was insufficient to use the materials for plants in chemical industries, and an improvement in such a property was also required.

In view of the above-described situation, an object of the present invention is to provide an Fe-Cr alloy which has an improved workability as well as an excellent high-temperature strength.

Another object of the present invention is to provide an Fe-Cr alloy which has sufficient acid resistance and/or oxidation resistance in addition to the improved workability and high-temperature resistance.

5 In order to achieve the above-described objects, the inventors of the present invention have made an extensive study and surprisingly found that an Fe-Cr alloy wherein the contents of impurities including C, N, O, P and S, which had been present in conventional Fe-Cr alloys, are reduced to an extremely low level would have a markedly superior ductility. Furthermore, the inventors of the present invention found that high-temperature strength of the resulting product may be significantly improved by adding a predetermined amount of at least one member selected from Ti, Nb, Zr, V, Ta, W and B to the above-mentioned Fe-Cr alloy of a reduced impurity content. The present invention has been achieved on the basis of such findings.

According to the present invention, there is provided an Fe-Cr alloy having excellent workability and high-temperature strength characterized in that the alloy comprises 3 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt \%} \quad (1);$$

20 the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, high-temperature strength, and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$25 \quad 0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt \%} \quad (1);$$

and at least one member selected from Ni, Co and Cu at a content that meets the following relation (2):

$$30 \quad 0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (2);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, high-temperature strength, and oxidation resistance characterized in that the alloy comprises 3 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt \%} \quad (1);$$

40 and at least one member selected from Al, Si and Mn at a content that meets the following relation (3):

$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (3),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

$$45 \quad 0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (4);$$

the balance being Fe and inevitable impurities.

50 According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, high-temperature strength, acid resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$55 \quad 0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt \%} \quad (1);$$

at least one member selected from Ni, Co and Cu at a content that meets the following relation (2):

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$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (2);$$

and at least one member selected from Al, Si and Mn at a content that meets the following relation (3):

5 $0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (3),$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

10 $0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (4);$

the balance being Fe and inevitable impurities.

[C] Inventions of category C

15

The Fe-Cr alloys as described above contain a relatively large amount of Cr since corrosion resistance is of prime importance in these alloys. As a result, these alloys occasionally suffer from poor ductility, and hence, insufficient workability. When such materials are used in such application as automobile exterior material or a building exterior material wherein the material is required to have a sufficient workability, they may suffer from such problems as cracking upon working, or an extreme difficulty in working due to strict working conditions. As set forth above, there is, a strong demand for an improvement of such materials in their workability.

Furthermore, the corrosion resistance of such materials is yet insufficient for such applications as automobile exterior materials or building exterior materials wherein pitting resistance is required, and structural materials for chemical plants wherein acid resistance is additionally required.

Still further, such materials are still insufficient in their strength and oxidation resistance at a high temperature to use the materials for such applications as automobile exhaust gas pipes wherein the material is exposed to a high temperature. Accordingly, there is also a demand for a further improvement in such properties.

30 In view of the above-described situation, main object of the present invention is to provide an Fe-Cr alloy which has an improved workability as well as a sufficient pitting resistance.

Another object of the present invention is to provide an Fe-Cr alloy which has an improved acid resistance in addition to the above-mentioned improved properties.

35 A further object of the present invention is to provide an Fe-Cr alloy which has an improved oxidation resistance in addition to the improved workability and acid resistance.

In order to achieve the above-described objects, the inventors of the present invention have made an extensive study and surprisingly found that an Fe-Cr alloy wherein the contents of impurities including C, N, O, P and S, which had been present in conventional Fe-Cr alloys, are reduced to an extremely low level would have a markedly superior ductility in addition to a sufficient corrosion resistance.

40 Furthermore, the inventors of the present invention found that pitting resistance of the resulting product may be significantly improved by adding a predetermined amount of Mo to the above-mentioned Fe-Cr alloy of a reduced impurity content, and that acid resistance of the resulting product may be significantly improved by further addition of at least one member selected from Ni, Co and Cu in a predetermined amount.

45 Still further, the inventors of the present invention found that oxidation resistance of the resulting product may be significantly improved by further addition of a predetermined amount of at least one member selected from Al, Si and Mn and/or a predetermined amount of at least one member selected from Ca, Mg and REM. The present invention has been completed on the basis of such finding.

50 According to the present invention, there is provided an Fe-Cr alloy having excellent workability and pitting resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and 0.5 to 20% by weight of Mo; the balance being Fe and inevitable impurities.

55 According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, pitting resistance, and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; and at least one member selected from Ni, Cu and Co at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, pitting resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; and at least one member selected from Al, Si and Mn at a content that meets the following relation (2):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (2),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (3);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, pitting resistance, acid resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ni, Cu and Co at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (1);$$

and at least one member selected from Al, Si and Mn at a content that meets the following relation (2):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (2),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (3);$$

the balance being Fe and inevitable impurities.

[D] Inventions of category D

The Fe-Cr alloys as described above contain a relatively large amount of Cr since corrosion resistance is of prime importance in these alloys. As a result, these alloys may occasionally suffer from poor ductility, and hence, insufficient workability. When such materials are used in such application as a basin compartment of a home kitchen sink, a building exterior material or an automobile exterior material wherein the material is required to have a sufficient workability, they may suffer from such problems as cracking upon working, or an extreme difficulty in working when strict working conditions are required. As set forth above, there is a strong demand for an improvement of such materials in their workability.

Furthermore, the corrosion resistance of such materials is yet insufficient for such applications as can body of a water heater and automobile muffler wherein pitting resistance and weld zone-corrosion resistance (intergranular corrosion resistance) are required, and chemical plants wherein acid resistance is additionally required.

In view of the above-described situation, first object of the present invention is to provide an Fe-Cr alloy which has an improved workability as well as sufficient pitting resistance and weld-zone corrosion resistance.

Second object of the present invention is to provide an Fe-Cr alloy which has an improved acid resistance and/or oxidation resistance in addition to the above-mentioned improved properties.

In order to achieve the above-described objects, the inventors of the present invention have made an extensive study and surprisingly found that an Fe-Cr alloy wherein the contents of impurities including C, N, O, P and S, which had been present in conventional Fe-Cr alloys, are reduced to an extremely low level would have a markedly superior ductility in addition to a sufficient corrosion resistance.

Furthermore, the inventors of the present invention found that pitting resistance of the resulting product may be significantly improved by adding a predetermined amount of Mo to the above-mentioned Fe-Cr alloy of a reduced impurity content, and that weld zone-corrosion resistance (intergranular corrosion

resistance) may be significantly improved by further addition of at least one member selected from Ti, Nb, Zr, V, Ta, W and B in a predetermined amount.

Still further, the inventors of the present invention found that acid resistance of the resulting product may be significantly improved by further addition of at least one member selected from Ni, Co and Cu in a predetermined amount. The inventors of the present invention also found that oxidation resistance of the resulting product may be significantly improved by further addition of a predetermined amount of at least one member selected from Si, Mn and Al and/or a predetermined amount of at least one member selected from Ca, Mg and REM. The present invention is based on such a series of findings.

According to the present invention, there is provided an Fe-Cr alloy having excellent workability, pitting resistance, and weld corrosion resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; and at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt } \% \quad (1);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, pitting resistance, weld corrosion resistance, and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt } \% \quad (1);$$

and at least one member selected from Ni, Cu and Co at a content that meets the following relation (2):

$$0.01 \text{ wt } \% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt } \% \quad (2);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, pitting resistance, weld corrosion resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt } \% \quad (1);$$

and at least one member selected from Si, Mn and Al at a content that meets the following relation (3):

$$0.1 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt } \% \quad (3);$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

$$0.001 \text{ wt } \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt } \% \quad (4);$$

the balance being Fe and inevitable impurities.

According to the present invention, there is also provided an Fe-Cr alloy having excellent workability, pitting resistance, weld corrosion resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt } \% \quad (1);$$

at least one member selected from Ni, Cu and Co at a content that meets the following relation (2):

$$0.01 \text{ wt } \% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt } \% \quad (2);$$

and at least one member selected from Si, Mn and Al at a content that meets the following relation (3):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (3),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (4);$$

the balance being Fe and inevitable impurities.

BRIEF DESCRIPTION OF THE DRAWINGS

- FIG. 1 diagrammatically illustrates tensile properties in relation to the total content of C, N, O, P and S.
 FIG. 2 diagrammatically illustrates corrosion rate in relation to the total content of C, N, O, P and S.
 FIG. 3 diagrammatically illustrates corrosion rate in relation to the Cr content.
 FIG. 4 diagrammatically illustrates corrosion rate in relation to (Ni + Co + 2Cu).
 FIG. 5 diagrammatically illustrates abnormally oxidized area in relation to the total content of C, N, O, P and S.
 FIG. 6 diagrammatically illustrates weight increase due to oxidation in relation to the Cr content.
 FIG. 7 diagrammatically illustrates abnormally oxidized area in relation to the value of (3Al + 2Si + Mn) (% by weight).
 FIG. 8 diagrammatically illustrates area of the oxide film that was peeled in relation to the value of (4Ca + 4Mg + REM) (% by weight).
 FIG. 9 diagrammatically illustrates tensile properties in relation to the total content of C, N, O, P and S for a series of Fe-18% Cr alloys.
 FIG. 10 diagrammatically illustrates increase in high-temperature proof stress in relation to (Ti + Nb + Zr + V + Ta + W + 50B).
 FIG. 11 diagrammatically illustrates corrosion rate in relation to the total content of C, N, O, P and S.
 FIG. 12 diagrammatically illustrates corrosion rate in relation to the Cr content.
 FIG. 13 diagrammatically illustrates corrosion rate in relation to (Ni + Co + 2Cu).
 FIG. 14 diagrammatically illustrates corrosion rate in relation to (Ti + Nb + Zr + V + Ta + W + 50B).
 FIG. 15 diagrammatically illustrates weight decrease in oxidation test in relation to the Cr content.
 FIG. 16 diagrammatically illustrates oxidation resistance in relation to (3Al + 2Si + Mn).
 FIG. 17 diagrammatically illustrates oxidation resistance in relation to (4Ca + 4Mg + REM).
 FIG. 18 diagrammatically illustrates tensile properties in relation to the total content of C, N, O, P and S.
 FIG. 19 diagrammatically illustrates pitting potential in relation to the Mo content.
 FIG. 20 diagrammatically illustrates acid resistance in relation to (Ni + Co + 2Cu) in % by weight.
 FIG. 21 diagrammatically illustrates oxidation resistance in relation to (3Al + 2Si + Mn).
 FIG. 22 diagrammatically illustrates oxidation resistance in relation to (4Ca + 4Mg + REM).
 FIG. 23 diagrammatically illustrates tensile properties in relation to the total content of C, N, O, P and S.
 FIG. 24 diagrammatically illustrates pitting potential in relation to the Mo content.
 FIG. 25 diagrammatically illustrates intergranular corrosion resistance in relation to (Ti + Nb + Zr + V + Ta + W + 50 x B) in % by weight.
 FIG. 26 diagrammatically illustrates acid resistance in relation to (Ni + Co + 2Cu) in % by weight.
 FIG. 27 diagrammatically illustrates oxidation resistance in relation to (3Al + 2Si + Mn).
 FIG. 28 diagrammatically illustrates oxidation resistance in relation to (4Ca + 4Mg + REM).

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention comprises four categories of inventions as described below. Description will be given in accordance with the order of the categories. The description is also given in accordance with the order of the categories in the sections of "Summary of the invention", "Examples", and "Industrial Utility".

[Inventions of Category A]

The inventions of this category claim priority on Japanese Patent Application Nos. 4-111014, 4-117358, and 4-128751; and correspond to claims 1 to 4, and FIGS. 1 to 8.

[Inventions of Category B]

The inventions of this category claim priority on Japanese Patent Application Nos. 4-128751, 4-141653, and 4-141655; and correspond to claims 5 to 8, and FIGS. 9 to 17.

[Inventions of Category C]

The inventions of this category claim priority on Japanese Patent Application Nos. 4-111430, and 4-141656; and correspond to claims 9 to 12, and FIGS. 18 to 22.

[Inventions of Category D]

The inventions of this category claim priority on Japanese Patent Application No. 4-112522; and correspond to claims 13 to 16, and FIGS. 23 to 28.

[A] Inventions of Category A

The present invention is hereinafter described in further detail.

(I) The Fe-Cr alloy of the present invention which has an improved workability is described below.

FIG. 1 diagrammatically shows increase in elongation and decrease in proof stress (yield strength) evaluated by tensile test (JIS Z-2241) in relation to the total content of C, N, O, P and S for a series of annealed cold rolled Fe-18% Cr alloy plates. As apparent from FIG. 1, the alloy plate would have a significantly superior ductility when the total content of C, N, O, P and S is 100 ppm or less.

In FIG. 1, increase in elongation (%) and decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm. The tensile properties used for such calculation are:

Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

elongation: 25%

proof stress: 450 N/mm²

The Fe-Cr alloy of the present invention contains C, N, O, P and S in a total content of 100 ppm or less. As described above, the alloy plate has a significantly improved ductility, and hence, workability when the total content of C, N, O, P and S is 100 ppm or less. On the other hand, the alloy plate will have a reduced ductility, and hence, a reduced workability as the total content of C, N, O, P and S exceeds 100 ppm.

Furthermore, the Fe-Cr alloy of the present invention has a Cr content of from 3 to 60% by weight, and preferably, from 5 to 30% by weight. The Cr content of less than 3% by weight will result in a poor corrosion resistance, while the Cr content in excess of 60% by weight will result in an insufficient workability even when the content of C, N, O, P and S is reduced.

In other words, an Fe-Cr alloy having a total content of C, N, O, P and S of up to 100 ppm and a Cr content of from 3 to 60% by weight would have a significantly improved workability as well as a sufficient corrosion resistance.

The alloy of the present invention may also have such an additional element as Al, Mo, Nb, B, Si, Mn, Cu, Ni, Co, or Ca added thereto.

In the production of the Fe-Cr alloy of the present invention, a high-purity electrolytic iron and a high-purity electrolytic chromium may be employed as the starting materials. The optionally added element is also added in its high purity form. The primary impurity is oxygen regardless of the type of the starting material, and therefore, in the production of the Fe-Cr alloy of the present invention, melting and casting are carried out under an ultra-high vacuum of 10⁻⁷ torr or less.

The alloy of the present invention will exert its merits whether the product is an annealed hot rolled plate or an annealed cold rolled plate, and in addition, whether the surface finishing of the annealed cold rolled plate is BA, 2B, 2D, HL or ground finish.

- 5 (II) The Fe-Cr alloy of the present invention which has an improved workability as well as an excellent acid resistance is described below.

FIG. 2 diagrammatically shows corrosion rate in relation to the total content of C, N, O, P and S for a series of alloy plates comprising Fe - 36% Cr - 3.2% Co. As apparent from FIG. 2, the alloy plate would exhibit a significantly low degree of corrosion when the total content of C, N, O, P and S is 100 ppm or less.

FIG. 3 diagrammatically shows corrosion rate in relation to Cr content for two series of alloy plates comprising Fe - Cr - 1.6% Ni - 1.4% Co respectively having a total content of C, N, O, P and S of 100 ppm or less and in excess of 100 ppm. As apparent from FIG. 3, the corrosion rate is significantly low in the alloys having the total content of C, N, O, P and S of 100 ppm or less compared to the alloys having the total content of C, N, O, P and S in excess of 100 ppm, and such difference in the corrosion resistance is even more significant when the Cr content is 5% by weight or more.

FIG. 4 diagrammatically shows corrosion rate in relation to (Ni + Co + 2Cu) for a series of alloy plates comprising Fe - 38% Cr having the total content of C, N, O, P and S of 62 ppm. As apparent from FIG. 4, the corrosion rate would rapidly decrease when the (Ni + Co + 2Cu) value reaches 0.01% by weight.

The components constituting the alloy of the present invention is hereinafter described in detail.

Cr: Cr content is limited to the range of from 5 to 60% by weight, and preferably, from 10 to 40% by weight. As described above, the alloy having the Cr content within such a range would exhibit a sufficient acid resistance. Addition of an excessive amount of the Cr would result in poor workability. In addition, such an excessive addition of the Cr would not contribute to further improvement in the acid resistance.

C, N, O, P and S: These elements are contained in total content of 100 ppm or less, and preferably in the total content of 85 ppm or less. As described above, the alloy plate would exhibit an improved acid resistance as well as an excellent workability when the total content of C, N, O, P and S is 100 ppm or less and other conditions are also satisfied.

Cu, Ni, Co: All of these elements are effective and essential for improving the acid resistance of the alloy. The alloy of the present invention contains at least one member selected from these elements in an amount that meets the following relation:

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1),$$

and preferably, in an amount that meets the following relation:

$$0.05 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5.0 \text{ wt \%} \quad (1a).$$

A content of Ni, Co and Cu less than the above-defined range would result in an insufficient corrosion resistance, and a content in excess of the above-defined range would result in a reduced production efficiency of the alloy.

Preferred content for each of the Ni, Co and Cu are as described below in view of the above-described reasons.

- Ni: 0.05 to 5.0% by weight
Co: 0.05 to 5.0% by weight
Cu: 0.05 to 2.5% by weight

The Fe-Cr alloys satisfying the above-described conditions would have a significantly improved corrosion resistance in addition to an excellent workability.

In the production of the Fe-Cr alloy of the present invention having an improved workability as well as an excellent acid resistance, an ultra high-purity electrolytic iron, an electrolytic Cr, an electrolytic Ni, an electrolytic Cu, an electrolytic Co, an iodide-processed Ti, an electrolytically reduced Nb, a molten salt electrolytic Zr, a reduced V, an electrolytic Ta, an electrolytically reduced W, and a high purity ferroboron may be employed for the starting materials.

The primary impurity is oxygen regardless of the type of the component, and therefore, melting and casting may be carried out under an ultra-high vacuum of 10^{-5} torr or less, and preferably, 10^{-7} torr or less for the production of the Fe-Cr alloy of the present invention.

(III) The Fe-Cr alloy of the present invention which has an improved workability as well as an excellent oxidation resistance is described below.

FIG. 5 diagrammatically shows abnormally oxidized area in a continuous oxidation test in relation to the total content of C, N, O, P and S for a series of alloys comprising Fe - 24% Cr - 0.01% REM (Y: 0.05%; La: 0.03%; Ce: 0.02%). As apparent from FIG. 5, the abnormally oxidized area would be very small when the total content of C, N, O, P and S is 100 ppm or less.

FIG. 6 diagrammatically shows weight increase in an oxidation test in relation to Cr content for a series of Fe-Cr-Al alloys. As apparent from FIG. 6, the weight increase in the oxidation would significantly decrease when the Cr content is 3.0% by weight or more when the total content of C, N, O, P and S is 100 ppm or less.

FIG. 7 diagrammatically shows abnormally oxidized area in a continuous oxidation test in relation to the value of (3Al + 2Si + Mn) for a series of Fe - 28% Cr alloys having the total content of C, N, O, P and S of 51 ppm. As apparent from FIG. 7, the abnormally oxidized area would significantly decrease when the (3Al + 2Si + Mn) value is 0.1% by weight or more.

FIG. 8 diagrammatically shows percentage of the area of the oxide film that was peeled in a repeated-heating test in relation to the value of (4Ca + 4Mg + REM) for a series of Fe - 26% Cr alloys having the total content of C, N, O, P and S of 72 ppm. As apparent from FIG. 8, the oxide film-peeled area would significantly decrease when the (4Ca + 4Mg + REM) value is 0.001% by weight or less.

The composition of the alloy according to this invention and aspects of the invention are described below. The Fe-Cr alloy of the present invention having an improved workability as well as an excellent oxidation resistance has three aspects as described below.

(1) First Aspect of the Invention

Cr: Cr content is limited to the range of from 3 to 60% by weight, and preferably, from 10 to 40% by weight. When the Cr content is within such a range and other conditions are also satisfied, the resulting alloy would have a sufficient oxidation resistance. Addition of the Cr in excess of such an amount is likely to induce a decrease in workability, and would not contribute to further improvement in the oxidation resistance.

C, N, O, P and S: These elements are contained in total content of 100 ppm or less, and preferably, 85 ppm or less. Abnormal oxidation is avoided when such conditions are satisfied. Such conditions in association with other conditions would result in an alloy having an improved oxidation resistance as well as an excellent ductility, and hence, high workability.

Si, Mn, Al: The alloy of the first aspect of the invention contains at least one such metal in an amount that meets the following relation (2):

$$0.1 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt } \% \quad (2),$$

and preferably, in an amount that meets the following relation (2a):

$$0.5 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 25 \text{ wt } \% \quad (2a).$$

When the content is within such a range and other conditions are also satisfied, the resulting alloy would have a significantly improved oxidation resistance. These elements should not be contained in an excess amount since the elements contained such that the (3Al + 2Si + Mn) value is in excess of the range of relation (2) would render the alloy production difficult.

Preferably, the elements are respectively contained in the amounts as described below for the reasons as noted below.

Si: 0.1 to 10.0% by weight

Inclusion of less than 0.1% by weight is not significantly effective. Inclusion in excess of 10.0% by weight would result in a significantly decreased produceability.

Mn: 0.1 to 5.0% by weight

Inclusion of less than 0.1% by weight is not significantly effective. Inclusion in excess of 5% by weight would result in a significantly decreased produceability.

Al: 0.1 to 4.0% by weight

Inclusion of less than 0.1% by weight is not significantly effective. Inclusion in excess of 4.0% by weight would result in a significantly decreased produceability.

An Fe-Cr alloy which meets the above-described conditions would have an improved oxidation resistance as well as excellent workability, and therefore, such an alloy may be adequately used for producing various components in automobile exhaust gas system or various pipes used under the conditions of repeated high temperature oxidation.

(2) Second Aspect of the Invention

With regard to the Cr content, the content of C, N, O, P, and S, and the Fe content, what has been described for the alloy according to the first aspect of the invention applies to the alloy according to the second aspect of the invention.

The alloy according to the second aspect of the invention comprises at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (3):

$$0.001 \text{ wt } \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt } \% \quad (3),$$

and preferably, in an amount that meets the following relation (3a):

$$0.005 \text{ wt } \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.15 \text{ wt } \% \quad (3a).$$

When the content is within such a range and other conditions are also satisfied, the resulting alloy would have a sufficient oxidation resistance as well as an excellent workability.

These elements are significantly effective in improving the protectability of the oxide film formed on the surface of the alloy according to the second aspect of the invention, and hence, in suppressing the abnormal oxidation which is likely to take place in an extremely thin material. The elements also improve adhesion of the oxide film to the underlying material.

An excessive inclusion of these elements to an amount such that the $(4\text{Ca} + 4\text{Mg} + \text{REM})$ value is in excess of 0.2% by weight is undesirable since such an addition is likely to result in surface defects of the resulting alloy.

Preferably, Ca, Mg and the rare earth metal are respectively contained in the amounts as described below for the reasons as noted below.

Ca: 0.002 to 0.01% by weight

Inclusion of less than 0.002% by weight is not significantly effective. Inclusion in excess of 0.01% by weight would result in a significantly decreased produceability.

Mg: 0.002 to 0.01% by weight

Inclusion of less than 0.002% by weight is not significantly effective. Inclusion in excess of 0.01% by weight would result in a significantly decreased produceability.

Rare earth metal: 0.005 to 0.1% by weight

Inclusion of less than 0.005% by weight is not significantly effective. Inclusion in excess of 0.1% by weight would result in a significantly decreased produceability.

The alloy according to the second aspect of the invention may be used for applications similar to those of the alloy according to the first aspect of the invention.

(3) Third Aspect of the Invention

The alloy according to the third aspect of the invention comprises an alloy which meets the conditions for both the alloys according to the first and the second aspects of the invention, namely, an alloy having a Cr content of from 3 to 60% by weight; a total content of C, N, O, P and S of up to 100 ppm; a content of at least one member selected from Si, Mn and Al in the range that meets the above-mentioned relation (2); and a content of at least one member selected from Ca, Mg, and rare earth metals (REM) in the range that meets the above-mentioned relation (3). Such an alloy has an excellent workability as well as an oxidation resistance even superior to that of the alloy according to the first or the second aspect of the invention, and therefore, may be appropriately used for any of the above-mentioned applications.

In the production of the Fe-Cr alloy of the present invention including the above-described three aspects, an ultra high-purity electrolytic iron, an electrolytic chromium, a zone melting-processed silicon, a molten salt-electrolytic manganese, a molten salt-electrolytic aluminum, a molten salt-electrolytic calcium, an electrolytically reduced magnesium, and an electrolytically reduced rare earth metal may be employed as the starting materials. The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting are carried out under an ultra-high vacuum of 10^{-5} torr or less for the

production of the Fe-Cr alloy of the present invention.

(IV) The Fe-Cr alloy of the present invention which has an excellent acid resistance and oxidation resistance in addition to an improved workability is described below.

5

The alloy of this invention comprises the alloy of particularly excellent acid resistance described in the above (II) having added thereto the components of the alloy of particularly improved oxidation resistance described in the above (III). In view of such situation, the alloy of this invention is hereinafter described merely for its composition, and detailed description for each alloy component is omitted since it is the same as the one given in (II) and (III).

10

As in the case of (III), this invention comprises three aspects. The content of C + N + O + S + P is up to 100 ppm, and the Cr content is from 5 to 60% by weight in all three aspects of the invention. The components which may vary are described below for each aspect.

15

(1) First Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (1):

20

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1),$$

and preferably, in an amount that meets the following relation:

25

$$0.05 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5.0 \text{ wt \%} \quad (1a).$$

The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (2):

30

$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (2),$$

and preferably, in an amount that meets the following relation:

$$0.5 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 25 \text{ wt \%} \quad (2a).$$

35

(2) Second Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (1):

40

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1),$$

and preferably, in an amount that meets the following relation:

45

$$0.05 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5.0 \text{ wt \%} \quad (1a).$$

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (3):

50

$$0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (3),$$

and preferably, in an amount that meets the following relation:

$$0.005 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.15 \text{ wt \%} \quad (3a).$$

55

(3) Third Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (1):

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$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1),$$

and preferably, in an amount that meets the following relation:

$$0.05 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5.0 \text{ wt \%} \quad (1a).$$

The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (2):

$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (2),$$

and preferably, in an amount that meets the following relation:

$$0.5 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 25 \text{ wt \%} \quad (2a).$$

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (3):

$$0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (3),$$

and preferably, in an amount that meets the following relation:

$$0.005 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.15 \text{ wt \%} \quad (3a).$$

The process for producing the alloy of this invention is the same as the above-described processes, and therefore, detailed description of the production process is omitted.

[B] Inventions of Category B

The present invention is hereinafter described in further detail.

(I) The Fe-Cr alloy of the present invention which has an improved workability as well as an excellent high temperature strength is described below.

FIG. 9 diagrammatically shows results of tensile test at room temperature in relation to the total content of C, N, O, P and S for a series of Fe-18% Cr alloy plates by using the results for a conventional alloy plate having a total content of C, N, O, P and S of about 500 ppm as a reference. As apparent from FIG. 9, the alloy plate would exhibit a significantly increased elongation as well as a significantly decreased yield strength to indicate a markedly improved ductility when the total content of C, N, O, P and S is 100 ppm or less, as compared to the conventional alloy. In FIG. 9, increase in elongation (%) and decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm.

The tensile properties used for such calculation are:

Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

elongation: 25%

proof stress: 450 N/mm²

FIG. 10 diagrammatically shows increase in high temperature proof stress (at 900 °C) in relation to the value of (Ti + Nb + Zr + V + Ta + W + 50B). As apparent from FIG. 10, the high temperature strength would increase by 0.1 N/mm² and the alloy material would have a significantly improved high temperature strength when the above-defined value reaches 0.01% by weight.

The composition of the alloy according to this invention is hereinafter described in detail.

Cr: Cr content is limited to the range of from 3 to 60% by weight, and preferably, from 5 to 45% by weight. When the Cr content is within such a range and other conditions are satisfied, the resulting alloy

plate would have a sufficient oxidation resistance. Addition of the Cr in excess of 60% by weight is undesirable in view of an increased cost.

C, N, O, P and S: These elements are contained in a total content of 100 ppm or less, and preferably, 85 ppm or less. When the content is limited to such a range, the resulting alloy would have an improved ductility, and hence, workability, and the resulting alloy would also have an improved oxidation resistance when the Cr content is within the above-defined range. When the content is in excess of 100 ppm, the resulting alloy would not have such improved properties.

Ti, Nb, Zr, V, Ta, W and B: The alloy of the present invention contains at least one element selected from Ti, Nb, Zr, V, Ta, W and B in an amount that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50 \times \text{B} \leq 6 \text{ wt } \% \quad (1),$$

and preferably, in an amount that meets the following relation (1a):

$$0.1 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50 \times \text{B} \leq 4 \text{ wt } \% \quad (1a).$$

The alloy of the present invention containing such elements in an amount within the above-defined range has a significantly improved high temperature strength. However, an addition of such elements in excess of the range defined by (1) may lead to an increased brittleness although the high temperature strength would be maintained at the sufficient level.

Preferably, the Ti, Nb, Zr, V, Ta, W and B may respectively have the following contents:

Ti:	Ti \leq 5 (C% + N%)
Nb:	0.01 to 1% by weight
Zr:	0.01 to 1% by weight
V:	0.02 to 1% by weight
Ta:	0.01 to 1% by weight
W:	0.03 to 1% by weight, and
B:	0.0003 to 0.3% by weight.

An alloy which meets the above-described conditions would have an improved workability as well as a sufficient high temperature strength, and therefore, would be adequate for such applications as an automobile exhaust gas pipe, wherein the alloy material made into a pipe should be subsequently bent.

In the production of the above-described Fe-Cr alloy of (I) according to the present invention, an ultra high-purity electrolytic iron and an electrolytic Cr are employed for the starting materials.

The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting may be carried out under such an ultra-high vacuum as 10^{-5} torr or less for the production of the Fe-Cr alloy of the present invention.

(II) The Fe-Cr alloy of the present invention which has an improved workability as well as excellent high temperature strength and acid resistance is described below.

FIG. 9 diagrammatically shows results of tensile test at room temperature in relation to the total content of C, N, O, P and S for a series of Fe-18% Cr alloy plates by using the results for a conventional alloy plate having a total content of C, N, O, P and S of about 500 ppm as a reference. As apparent from FIG. 9, the alloy plate would exhibit a significantly increased elongation as well as a significantly decreased yield strength to indicate a markedly improved ductility when the total content of C, N, O, P and S is 100 ppm or less, as compared to the conventional alloy.

FIG. 10 diagrammatically shows increase in high temperature proof stress (at 900°C) in relation to the value of (Ti + Nb + Zr + V + Ta + W + 50B). As apparent from FIG. 10, the high temperature proof stress would increase by 0.1 N/mm² and the alloy material would have a significantly improved high temperature strength when the above-defined value reaches 0.01% by weight.

FIG. 11 diagrammatically shows corrosion rate in relation to the total content of C, N, O, P and S for a series of alloy plates comprising Fe - 36% Cr - 3.2% Co. As apparent from FIG. 11, the alloy plate would exhibit a significantly low degree of corrosion when the total content of C, N, O, P and S is 100 ppm or less.

FIG. 12 diagrammatically shows corrosion rate in relation to Cr content for two series of alloy plates comprising Fe - Cr - 1.6% Ni - 1.4% Co respectively having a total content of C, N, O, P and S of 100 ppm or less and in excess of 100 ppm. As apparent from FIG. 12, the corrosion rate is significantly low in the alloys having the total content of C, N, O, P and S of 100 ppm or less compared to the alloys having the total content of C, N, O, P and S in excess of 100 ppm, and such difference in the corrosion resistance is

even more significant when the Cr content is 5% by weight or more.

FIG. 13 diagrammatically shows corrosion rate in relation to (Ni + Co + 2Cu) for a series of alloy plates comprising Fe - 38% Cr having the total content of C, N, O, P and S of 62 ppm. As apparent from FIG. 13, the corrosion rate would rapidly decrease when the (Ni + Co + 2Cu) value reaches 0.01% by weight.

FIG. 14 diagrammatically shows corrosion rate in relation to the value of (Ti + Nb + Zr + Ta + V + W + 20B) (in % by weight) for a series of alloy plates comprising Fe - 46% Cr - 3.0% Co - 1.2% Cu having a total content of C, N, O, P and S of 64 ppm or less. As apparent from FIG. 14, corrosion rate would be significantly reduced when the above-defined value reaches 0.01%.

The composition of the alloy according to this invention is hereinafter described in detail.

Cr: Cr content is limited to the range of from 5 to 60% by weight, and preferably, from 10 to 40% by weight. As described above, the alloy having the Cr content within such a range would exhibit a sufficient acid resistance. Addition of an excessive amount of the Cr would result in poor workability. In addition, such an excessive addition of the Cr would not contribute to further improvement in the acid resistance.

C, N, O, P and S: These elements are contained in total content of 100 ppm or less, and preferably in the total content of 85 ppm or less. As described above, the alloy plate would exhibit an improved acid resistance as well as an excellent workability when the total content of C, N, O, P and S is 100 ppm or less and other conditions are also satisfied.

Ti, Nb, Zr, V, Ta, W and B: The alloy of the present invention contains at least one element selected from Ti, Nb, Zr, V, Ta, W and B in an amount that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50 \times \text{B} \leq 6 \text{ wt } \% \quad (1),$$

and preferably, in an amount that meets the following relation (1a):

$$0.1 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50 \times \text{B} \leq 4 \text{ wt } \% \quad (1a).$$

The alloy of the present invention containing such elements in an amount within the above-defined range has a significantly improved high temperature strength. However, an addition of such elements in excess of the range defined by (1) may lead to an increased brittleness although the high temperature strength would be maintained at the sufficient level.

Preferably, the Ti, Nb, Zr, V, Ta, W and B may respectively have the following contents:

Ti: Ti \leq 5 (C% + N%)
 Nb: 0.01 to 1% by weight
 Zr: 0.01 to 1% by weight
 V: 0.02 to 1% by weight
 Ta: 0.01 to 1% by weight
 W: 0.03 to 1% by weight, and
 B: 0.0003 to 0.3% by weight.

Cu, Ni, Co: All of these elements are effective and essential for improving the acid resistance of the alloy. The alloy of the present invention contain at least one member selected from these elements in an amount that meets the following relation:

$$0.01 \text{ wt } \% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt } \% \quad (2),$$

and preferably, in an amount that meets the following relation:

$$0.05 \text{ wt } \% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5.0 \text{ wt } \% \quad (2a).$$

A content of Ni, Co and Cu less than the above-defined range would result in an insufficient corrosion resistance, and a content in excess of the above-defined range would result in a reduced production efficiency of the alloy.

Preferred content for each of the Ni, Co and Cu are as described below in view of the above-described reasons.

Ni: 0.05 to 5.0% by weight
 Co: 0.05 to 5.0% by weight
 Cu: 0.05 to 2.5% by weight

The Fe-Cr alloys satisfying the above-described conditions would have a significantly improved

corrosion resistance in addition to an excellent workability.

In the production of the Fe-Cr alloy according to the present invention described in (II), an ultra high-purity electrolytic iron, an electrolytic Cr, an electrolytic Ni, an electrolytic Cu, an electrolytic Co, an iodide-processed Ti, an electrolytically reduced Nb, a molten salt electrolytic Zr, a reduced V, an electrolytic Ta, an electrolytically reduced W, and a high purity ferroboreon may be employed for the starting materials.

The primary impurity is oxygen regardless of the type of the component, and therefore, melting and casting may be carried out under an ultra-high vacuum of 10^{-5} torr or less, and preferably, 10^{-7} torr or less for the production of the Fe-Cr alloy of the present invention.

(III) The Fe-Cr alloy of the present invention which has an improved workability as well as excellent high temperature strength and oxidation resistance is described below.

FIG. 9 diagrammatically shows results of tensile test at room temperature in relation to the total content of C, N, O, P and S for a series of Fe-18% Cr alloy plates by using the results for a conventional alloy plate having a total content of C, N, O, P and S of about 500 ppm as a reference. As apparent from FIG. 9, the alloy plate would exhibit a significantly increased elongation as well as a significantly decreased yield strength to indicate a markedly improved ductility when the total content of C, N, O, P and S is 100 ppm or less, as compared to the conventional alloy.

FIG. 10 diagrammatically shows increase in high temperature proof stress (at 900°C) in relation to the value of $(\text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B})$. As apparent from FIG. 10, the high temperature proof stress would increase by 0.1 N/mm² and the alloy material would have a significantly improved high temperature strength when the above-defined value reaches 0.01% by weight.

FIG. 15 diagrammatically shows results of oxidation resistance test (weight loss upon scale removal after exposure to air at 1,350 K for 12 hours) for two series of Fe-Cr alloy plates respectively having a total content of C, N, O, P and S of 100 ppm or less and 100 ppm or more. As apparent from FIG. 15, when the total content of C, N, O, P and S is reduced to 100 ppm or less, the alloy containing 3% or more of Cr would have an oxidation resistance equivalent to that of the conventional steel having a Cr content of 12% or more to reveal effectiveness of the increased purity on the decrease in the Cr content, and hence, resources saving.

FIG. 16 diagrammatically shows results of oxidation resistance test (weight loss upon scale removal after exposure to air at 1,350 K for 12 hours) for a series of Fe-(15-30)% Cr alloy plates. As apparent from FIG. 16, the alloy containing 0.1% or more of $(3\text{Al} + 2\text{Si} + \text{Mn})$ would have an improved oxidation resistance.

FIG. 17 diagrammatically shows results of oxidation resistance test (weight loss upon scale removal after exposure to air at 1,350 K for 12 hours) for a series of Fe-(15-30)% Cr alloy plates. As apparent from FIG. 17, the alloy containing 0.001% or more of $(4\text{Ca} + 4\text{Mg} + \text{REM})$ would have an improved oxidation resistance.

The composition of the alloy according to this invention and aspects of the invention are described below. The Fe-Cr alloy of the present invention having an improved workability as well as excellent high temperature strength and oxidation resistance has three aspects as described below.

(1) First Aspect of the Invention

Cr: Cr content is limited to the range of from 3 to 60% by weight, and preferably, from 5 to 45% by weight. When the Cr content is within such a range and other conditions are satisfied, the resulting alloy plate would have a sufficient oxidation resistance. Addition of the Cr in excess of 60% by weight is undesirable in view of an increased cost.

C, N, O, P and S: These elements are contained in a total content of 100 ppm or less, and preferably, 85 ppm or less. When the content of the elements is limited to such a low range, the resulting alloy would have an improved ductility, and hence, workability, and the resulting alloy would also have an improved oxidation resistance when the Cr content is within the above-defined range. When the content is in excess of 100 ppm, the resulting alloy would not have such improved properties.

Ti, Nb, Zr, V, Ta, W and B: The alloy of the present invention contains at least one element selected from Ti, Nb, Zr, V, Ta, W and B in an amount that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt } \% \quad (1).$$

and preferably, in an amount that meets the following relation (1a):

$$0.1 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 4 \text{ wt } \% \quad (1a).$$

The alloy containing such elements in an amount within the above-defined range has a significantly improved high temperature strength. However, an addition of such elements in excess of the range defined by (1) may lead to an increased brittleness although the high temperature strength would be maintained at the sufficient level.

Preferably, the Ti, Nb, Zr, V, Ta, W and B may respectively have the following contents:

Ti:	Ti \leq 5 (C% by weight + N% by weight)
Nb:	0.01 to 1% by weight
Zr:	0.01 to 1% by weight
V:	0.02 to 1% by weight
Ta:	0.01 to 1% by weight
W:	0.03 to 1% by weight, and
B:	0.0003 to 0.3% by weight.

Al, Si, Mn: The alloy of the present invention contains at least one element selected from Al, Si and Mn in an amount that meets the following relation (3):

$$0.1 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt } \% \quad (3),$$

and preferably, in an amount that meets the following relation (3a):

$$0.3 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 30 \text{ wt } \% \quad (3a).$$

Inclusion in the alloy of such elements at a content within the above-defined range would result in an improved oxidation resistance of the resulting alloy. However, when these elements are added to such a content that $(3\text{Al} + 2\text{Si} + \text{Mn})$ exceeds 50% by weight, the resulting alloy would have an insufficient workability, and therefore, such an excessive inclusion is not preferred.

Preferably, Al, Si and Mn are respectively contained in the amounts as described below.

Al:	0.1 to 4% by weight
Si:	0.3 to 3% by weight
Mn:	0.5 to 10% by weight

(2) Second Aspect of the Invention

With regard to the Cr content, the content of C, N, O, P and S, and the preferable content of Ti, Nb, Zr, V, Ta, W and B, what has been described for the first aspect of the invention is applicable for the second aspect of the invention.

The alloy according to the second aspect of the invention comprises at least one member selected from Ca, Mg and rare earth metals (REM) as described below.

Ca, Mg, and REM: These elements are not critical for the alloy of the present invention. However, oxidation resistance of the alloy may be improved by including these elements in an amount that meets the following relation (4):

$$0.001 \text{ wt } \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt } \% \quad (4).$$

An excessive inclusion of these elements to an amount such that the $(4\text{Ca} + 4\text{Mg} + \text{REM})$ value is in excess of 0.2% by weight is undesirable since such an addition is likely to result in surface defects of the resulting alloy.

Preferably, Ca, Mg and the rare earth metal are respectively contained in the amounts as described below.

Ca:	0.0002 to 0.03% by weight
Mg:	0.0003 to 0.03% by weight
Rare earth metal:	0.0005 to 0.15% by weight

An alloy which meets the above-described conditions would have an improved workability as well as sufficient high temperature strength and oxidation resistance, and therefore, would be adequate for such applications as an automobile exhaust gas pipe, wherein the alloy material made into a pipe should be subsequently bent.

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In the production of the Fe-Cr alloy of the present invention, an ultra high-purity electrolytic iron and an electrolytic Cr are employed for the starting materials.

The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting may be carried out under such an ultra-high vacuum as 10^{-7} torr or less for the production of the Fe-Cr alloy of the present invention.

(3) Third Aspect of the Invention

The alloy according to the third aspect of the invention comprises an alloy which meets the conditions for both the alloys according to the first and the second aspects of the invention, namely, an alloy having a Cr content of from 3 to 60% by weight; a total content of C, N, O, P and S of up to 100 ppm; a content of at least one member selected from Ti, Nb, Zr, V, Ta, W and B in the range that meets the above-mentioned relation (1); a content of at least one member selected from Si, Mn and Al in the range that meets the above-mentioned relation (3); and a content of at least one member selected from Ca, Mg, and rare earth metals (REM) in the range that meets the above-mentioned relation (4). Such an alloy has an excellent workability as well as an oxidation resistance even superior to those of the alloy according to the first or the second aspect of the invention, and therefore, may be appropriately used for any of the above-mentioned applications.

In the production of the Fe-Cr alloy of the present invention including the above-described three aspects, an ultra high-purity electrolytic iron, an electrolytic chromium, a zone melting-processed silicon, a molten salt-electrolytic manganese, a molten salt-electrolytic aluminum, a molten salt-electrolytic calcium, an electrolytically reduced magnesium, and an electrolytically reduced rare earth metal may be employed as the starting materials. The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting are carried out under an ultra-high vacuum of 10^{-5} torr or less for the production of the Fe-Cr alloy of the present invention.

(IV) The Fe-Cr alloy of the present invention which has excellent acid resistance and oxidation resistance in addition to improved workability and high temperature strength is described below.

The alloy of this invention comprises the alloy of particularly excellent acid resistance described in the above (II) having added thereto the components of the alloy of particularly improved oxidation resistance described in the above (III). In view of such situation, the alloy of this invention is hereinafter described merely for its composition, and detailed description for each alloy component is omitted since it is the same as the one given in (II) and (III).

As in the case of (III), this invention comprises three aspects. The content of C + N + O + P is up to 100 ppm; the Cr content is from 5 to 60% by weight; and the content of Ti + Nb + Zr + V + Ta + W + 50B is 0.01 % to 6 % in all three aspects of the invention. The components which may vary are described below for each aspect.

(1) First Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (2):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (2).$$

The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (3):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (3).$$

(2) Second Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (2):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (2).$$

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (4):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (4).$$

(3) Third Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (2):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (2).$$

The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (3):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (3).$$

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (4):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (4).$$

The process for producing the alloy of this invention is the same as the above-described processes, and therefore, detailed description of the production process is omitted.

[C] Inventions of Category C

The present invention is hereinafter described in further detail.

(I) The Fe-Cr alloy of the present invention which has an improved workability as well as an excellent pitting resistance is described below.

FIG. 18 diagrammatically shows increase in elongation and decrease in yield strength evaluated by tensile tests in accordance with JIS Z-2241 in relation to the total content of C, N, O, P and S for a series of annealed cold rolled Fe-18% Cr alloy plates. As apparent from FIG. 18, the alloy would become soft when the total content of C, N, O, P and S is 100 ppm or less as evidenced by a significantly superior ductility and a significantly lower yield strength.

In FIG. 18, increase in elongation (%) and decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm. The tensile properties used for such calculation are:

Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

elongation: 25%

proof stress: 450 N/mm²

FIG. 19 diagrammatically shows pitting potential (measured in accordance with JIS G 0577) in relation to Mo content for a series of annealed cold rolled Fe - 16% Cr alloy plates having the total content of C, N, O, P and S of 100 ppm or less. As apparent from FIG. 19, the pitting potential would significantly increase when the Mo content is 0.5% by weight or more to result in an improved pitting resistance.

The composition of the alloy according to the present invention is hereinafter described.

Cr: Cr content is limited to the range of from 5 to 60% by weight, and preferably, from 10 to 40% by weight. When the Cr content is within such a range, the resulting alloy plate would have a sufficient corrosion resistance. Addition of the Cr in excess of such an amount lacks economic rationality since such an excessive addition would not contribute to further improvement in the corrosion resistance. Furthermore, addition of an excessive amount of Cr is undesirable since a decrease in workability is likely to be induced by solid-solution strengthening of the Cr itself even when (C + N + O + P + S) is limited to up to 100

ppm.

C, N, O, P and S: These elements are contained in total content of 100 ppm or less. As described above, the alloy plate would have a significantly improved ductility, and hence, improved workability when the total content of C, N, O, P and S is 100 ppm or less.

5 Mo: Mo content is limited to the range of from 0.5 to 20% by weight, and preferably, from 0.5 to 5% by weight. Mo added to an amount of 0.5% by weight or more will result in an improved pitting resistance. An excessive addition of Mo is undesirable from economic point of view.

An Fe-Cr alloy which meets the above-described conditions would have a significantly improved workability as well as a sufficient pitting resistance.

10

(II) The Fe-Cr alloy of the present invention which has an improved workability as well as excellent pitting resistance and acid resistance is described below.

15 FIG. 20 diagrammatically shows corrosion rate in 0.3 % by weight aqueous HCl solution in relation to (Ni + Co + 2Cu) in % by weight for a series of annealed cold rolled Fe - 16% Cr alloy plates having a total content of C, N, O, P and S of 100 ppm or less. As apparent from FIG. 20, the corrosion rate would significantly decrease when the (Ni + Co + 2Cu) value is 0.01% by weight or more to result in an improved acid resistance.

20 With regard to the content of Cr, C, N, O, P, S and Mo, what has been described in the above (I) applies to the alloy of (II). The alloy according to the aspect (II) of the invention further comprises at least one member selected from Ni, Cu and Co in an amount that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (1).$$

25 and preferably, in an amount that meets the following relation (1a):

$$0.1 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 4 \text{ wt\%} \quad (1a).$$

Such an alloy would have an excellent acid resistance in addition to the above-described properties.

30 An addition of the Ni, Co and Cu in excess of the amount represented by the relation (1) is undesirable since such an excessive addition of the Ni, Co and Cu, which are austenite stabilization elements, is inconvenient for formation of single-phase ferritic structure.

An alloy according to the aspect (II) of the invention which meets the above-described conditions would have an improved workability as well as sufficient pitting resistance and acid resistance.

35 In producing the Fe-Cr alloys described in the above (I) and (II) of the present invention, a high-purity electrolytic iron, an electrolytic Cr, a metallic Mo, an electrolytic Ni, an electrolytic Cu, and a metallic Co may be employed as the starting materials. The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting are carried out under an ultra-high vacuum of 10^{-7} torr or less for the production of the Fe-Cr alloy of the present invention.

40 The alloy of the present invention will fully exert its merits whether the product is an annealed hot rolled plate or an annealed cold rolled plate, and in addition, whether the final surface finishing is BA, 2B, 2D, HL or ground finish.

45 (III) The Fe-Cr alloy of the present invention which has improved workability, pitting resistance and oxidation resistance is described below.

FIG. 21 diagrammatically shows results of oxidation resistance test (weight loss upon scale removal after exposure to air at 1,350 K for 12 hours) for a series of Fe-(15-30)% Cr alloy plates. As apparent from FIG. 21, the alloy containing 0.1% or more of (3Al + 2Si + Mn) would have an improved oxidation resistance.

FIG. 22 diagrammatically shows results of oxidation resistance test (weight loss upon scale removal after exposure to air at 1,350 K for 12 hours) for a series of Fe-(15-30)% Cr alloy plates. As apparent from FIG. 22, the alloy containing 0.001% or more of (4Ca + 4Mg + REM) would have an improved oxidation resistance.

55 The composition of the alloy according to this invention and aspects of the invention are described below. The Fe-Cr alloy of the present invention having an improved workability as well as excellent pitting resistance and oxidation resistance has three aspects as described below.

(1) First Aspect of the Invention

Cr: Cr content is limited to the range of from 5 to 60% by weight, and preferably, from 5 to 45% by weight. When the Cr content is within such a range and other conditions are satisfied, the resulting alloy plate would have a sufficient oxidation resistance. Addition of the Cr in excess of 60% by weight is undesirable in view of an increased cost.

C, N, O, P and S: These elements are contained in a total content of 100 ppm or less, and preferably, 85 ppm or less. When the content is limited to such a range, the resulting alloy would have an improved ductility, and hence, workability, and the resulting alloy would also have an improved oxidation resistance when the Cr content is within the above-defined range. When the total content is in excess of 100 ppm, the resulting alloy would not have such improved properties.

Mo: The alloy of the present invention contains Mo in an amount of from 0.5 to 20% by weight, and preferably, in an amount of from 0.5 to 5% by weight. The alloy of the present invention containing Mo in an amount within such a range has a significantly improved pitting resistance. However, inclusion of the Mo in excess of 20% by weight may lead to an increased cost, and therefore, such an excessive inclusion is not preferable.

Al, Si, Mn: The alloy of the present invention contains at least one element selected from Al, Si and Mn in an amount that meets the following relation (2):

$$0.1 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt } \% \quad (2),$$

and preferably, in an amount that meets the following relation (2a):

$$0.3 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 30 \text{ wt } \% \quad (2a).$$

Inclusion in the alloy of such elements at a content within the above-defined range would result in an improved oxidation resistance of the resulting alloy. However, when these elements are added to such a content that $(3\text{Al} + 2\text{Si} + \text{Mn})$ exceeds 50% by weight, the resulting alloy would have an insufficient workability, and therefore, such an excessive inclusion is not preferred.

Preferably, Al, Si and/or Mn are respectively contained in the amounts as described below.

Al: 0.1 to 4% by weight
Si: 0.3 to 3% by weight
Mn: 0.5 to 10% by weight

(1) Second Aspect of the Invention

With regard to the Cr content, the content of C, N, O, P and S, and the Mo content, what has been described for the first aspect of the invention applies to this aspect of the invention.

The alloy according to this aspect of the invention contains at least one member selected from Ca, Mg and REM.

Ca, Mg, and REM: Oxidation resistance of the alloy may be improved by including these elements in an amount that meets the following relation (3):

$$0.001 \text{ wt } \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt } \% \quad (3).$$

Preferably, Ca, Mg and the rare earth metal are respectively contained in the amounts as described below.

Ca: 0.0002 to 0.03% by weight
Mg: 0.0003 to 0.03% by weight

Rare earth metal: 0.0005 to 0.15% by weight

An alloy according to the present invention as described in (II) which meets the above-described conditions would have an improved workability as well as sufficient pitting resistance and oxidation resistance, and therefore, would be adequate for such applications as an automobile exhaust gas pipe.

In the production of the Fe-Cr alloy of the present invention, an ultra high-purity electrolytic iron and an electrolytic Cr are employed as the starting materials.

The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting may be carried out under such an ultra-high vacuum as 10^{-7} torr or less for the production of the Fe-Cr alloy of the present invention.

(3) Third Aspect of the Invention

The alloy according to the third aspect of the invention comprises an alloy which meets the conditions for both the alloys according to the first and the second aspects of the invention, namely, an alloy having a
 5 Cr content of from 5 to 60% by weight; a total content of C, N, O, P and S of up to 100 ppm; a Mo content of from 0.5 to 20% by weight; a content of at least one member selected from Si, Mn and Al in the range that meets the above-mentioned relation (2); and a content of at least one member selected from Ca, Mg, and rare earth metals (REM) in the range that meets the above-mentioned relation (3). Such an alloy has an excellent workability as well as an oxidation resistance even superior to those of the alloy according to the
 10 first or the second aspect of the invention, and therefore, may be appropriately used for any of the above-mentioned applications.

In the production of the Fe-Cr alloy of the present invention including the above-described three aspects, an ultra high-purity electrolytic iron, an electrolytic chromium, a zone melting-processed silicon, a molten salt-electrolytic manganese, a molten salt-electrolytic aluminum, a molten salt-electrolytic calcium,
 15 an electrolytically reduced magnesium, and an electrolytically reduced rare earth metal may be employed as the starting materials. The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting are carried out under an ultra-high vacuum of 10^{-5} torr or less for the production of the Fe-Cr alloy of the present invention.

20 (IV) The Fe-Cr alloy of the present invention which has excellent acid resistance and oxidation resistance in addition to improved workability and pitting resistance is described below.

The alloy of this invention comprises the alloy of particularly excellent acid resistance described in the above (II) having added thereto the components of the alloy of particularly improved oxidation resistance
 25 described in the above (III). In view of such situation, the alloy of this invention is hereinafter described merely for its composition, and detailed description for each alloy component is omitted since it is the same as the one given in (II) and (III).

As in the case of (III), this invention comprises three aspects. The content of C + N + O + P is up to 100 ppm; the Cr content is from 5 to 60% by weight; the Mo content is from 0.5 to 20% by weight; and the
 30 content of Ni + Co + 2Cu is from 0.01% to 6% in all three aspects of the invention. The components which may vary are described below for each aspect.

(1) First Aspect of the Invention

35 The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1).$$

40 The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (2):

$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (2).$$

45 (2) Second Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (1):

50 $0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1).$

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (3):

55 $0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (3).$

(3) Third Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (1):

$$0.01 \text{ wt} \% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt} \% \quad (1).$$

The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (2):

$$0.1 \text{ wt} \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt} \% \quad (2).$$

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (3):

$$0.001 \text{ wt} \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt} \% \quad (3).$$

The process for producing the alloy of this invention is the same as the above-described processes, and therefore, detailed description of the production process is omitted.

[D] Inventions of Category D

The present invention is hereinafter described in further detail.

- (I) The Fe-Cr alloy of the present invention which has an improved workability as well as excellent pitting resistance and weld corrosion resistance is described below.

FIG. 23 diagrammatically shows results of tensile test at room temperature in relation to the total content of C, N, O, P and S for a series of Fe-18% Cr alloy plates by using the results for a conventional alloy plate having a total content of C, N, O, P and S of about 500 ppm as a reference. As apparent from FIG. 23, the alloy plate would exhibit a significantly increased elongation as well as a significantly decreased yield strength to indicate a markedly improved ductility when the total content of C, N, O, P and S is 100 ppm or less, as compared to the conventional alloy.

It should be noted that the test samples had been prepared and evaluated as described below.

Test sample: The test plate was prepared by melting and casting the starting materials in a 10 kg vacuum melting furnace, hot rolling the molten material into a plate of 4 mm thick, recrystallization-annealing and descaling the hot-rolled plate, cold rolling the plate to a thickness of 0.8 mm, and subjecting the cold rolled plate to recrystallization-annealing.

Evaluation: The test samples were evaluated by a tensile test according to JIS Z-2241. The test samples of L, X and C directions were prepared, and the elongation was calculated by $(L + C + 2 \times X) / 4$.

In FIG. 23, increase in elongation (%) and decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm.

The tensile properties used for such calculation are:

Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

elongation: 25%

proof stress: 450 N/mm²

FIG. 24 diagrammatically shows pitting potential in relation to Mo content for a series of annealed cold rolled Fe-16% Cr alloy plates having a total content of C, N, O, P and S of 100 ppm or less. As apparent from FIG. 24, the pitting potential would rapidly increase when the Mo content reaches 0.5% by weight to result in an improved pitting resistance.

It should be noted that the test samples had been prepared and evaluated as described below.

Test sample: The test plate was prepared by melting and casting the starting materials in a 10 kg vacuum melting furnace, hot rolling the molten material into a plate of 4 mm thick, recrystallization-annealing and descaling the hot-rolled plate, cold rolling the plate to a thickness of 0.8 mm, subjecting the cold rolled plate to recrystallization-annealing, and grinding the surface with Emery #800.

Evaluation: An anode polarization curve was depicted in accordance with JIS G 0577 in a solution of 1,000 ppm Cl^- . A potential corresponding to V_c 10 μA was determined to be the pitting potential.

FIG. 25 diagrammatically shows the results of a test for intergranular corrosion of TIG weld zone in relation to the value of $(\text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50 \times \text{B})$ (in % by weight) for a series of annealed cold rolled Fe-20% Cr alloy plates having a total content of C, N, O, P and S of 100 ppm or less. As apparent from FIG. 25, weld zone-corrosion resistance (intergranular corrosion resistance) would be significantly improved when the above-defined value reaches 0.01%.

It should be noted that the test samples had been prepared and evaluated as described below.

Test sample: The test plate was prepared by melting and casting the starting materials in a 10 kg vacuum melting furnace, hot rolling the molten material into a plate of 4 mm thick, recrystallization-annealing and descaling the hot-rolled plate, cold rolling the plate to a thickness of 0.8 mm, subjecting the cold rolled plate to recrystallization-annealing, and grinding the surface with Emery #500. The thus prepared plate was subjected to TIG welding (bead on) to prepare the test sample.

Evaluation: The test sample was subjected to a sulfuric acid-copper sulfate test in accordance with JIS G-0572, and then, to a weld zone-bend test ($r = 2t$, bending to 180°C) to evaluate for the presence or the absence of cracks.

FIG. 26 diagrammatically shows corrosion rate in 5 % by weight aqueous HCl solution in relation to $(\text{Ni} + \text{Co} + 2\text{Cu})$ in % by weight for a series of Fe-(24-25)% Cr alloy plates having the total content of C, N, O, P and S of 100 ppm or less. As apparent from FIG. 26, the corrosion rate would rapidly decrease when the $(\text{Ni} + \text{Co} + 2\text{Cu})$ value reaches 0.01% by weight to result in an improved acid resistance.

It should be noted that the test samples had been prepared and evaluated as described below.

Test sample: The test plate was prepared by melting and casting the starting materials in a 10 kg vacuum melting furnace, hot rolling the molten material into a plate of 4 mm thick, recrystallization-annealing and descaling the hot-rolled plate, cold rolling the plate to a thickness of 0.8 mm, subjecting the cold rolled plate to recrystallization-annealing, and grinding the surface with Emery #500.

The composition of the alloy according to this invention is hereinafter described in detail.

Cr: Cr content is limited to the range of from 5 to 60% by weight, and preferably, from 10 to 35% by weight. When the Cr content is within such a range, the resulting alloy plate would have a sufficient corrosion resistance. Addition of the Cr in excess of such an amount lacks economic rationality since such an excessive addition would not contribute to further improvement in the corrosion resistance. Furthermore, addition of an excessive amount of Cr is undesirable since a decrease in workability is likely to be induced.

C, N, O, P and S: These elements are contained in total content of 100 ppm or less. As described above, the alloy plate would have a significantly improved ductility, and hence, improved workability when the total content of C, N, O, P and S is 100 ppm or less.

Mo: Mo content is limited to the range of from 0.5 to 20% by weight, and preferably, from 1 to 10% by weight. Mo added to an amount of 0.5% by weight or more will result in an improved pitting resistance, while an excessive addition of Mo is undesirable from economic point of view.

Ti, Nb, Zr, V, Ta, W and B: The alloy of the present invention contains at least one element selected from Ti, Nb, Zr, V, Ta, W and B in an amount that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt } \% \quad (1),$$

and preferably, in an amount that meets the following relation (1a):

$$0.05 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 0.5 \text{ wt } \% \quad (1a).$$

The alloy of the present invention containing such elements in an amount within the range defined by such a relation has a significantly improved weld zone-corrosion resistance (intergranular corrosion resistance). However, an excessive addition of such elements is undesirable since a decrease in workability is likely to be induced by solid-solution strengthening of such elements themselves.

Preferably, the Ti, Nb, Zr, V, Ta, W and B may respectively have the following contents:

- Ti: $\text{Ti} \leq 5 (\text{C}\% + \text{N}\%)$
- Nb: 0.01 to 0.5% by weight
- Zr: 0.01 to 0.5% by weight
- V: 0.01 to 0.5% by weight
- Ta: 0.01 to 0.5% by weight
- W: 0.01 to 0.5% by weight, and
- B: 0.0003 to 0.01% by weight.

An Fe-Cr alloy which meets the above-described conditions would have a significantly improved workability as well as sufficient pitting resistance and weld zone-corrosion resistance (intergranular corrosion resistance), and therefore, would be adequate for a variety of applications including can body of a water heater and automobile muffler.

(II) The Fe-Cr alloy of the present invention which has an improved workability as well as excellent pitting resistance, weld zone-corrosion resistance (intergranular corrosion resistance), and acid resistance is described below.

An alloy comprising at least one member selected from Ni, Cu and Co in an amount that meets the following relation (2):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (2),$$

and preferably, in an amount that meets the following relation (2a):

$$0.05 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5 \text{ wt \%} \quad (2a)$$

in additions to the alloy components described in the above (I) would have an excellent acid resistance in addition to the above-described properties.

An addition of the Ni, Co and Cu in excess of the amount represented by the relation (2) is undesirable since such an excessive addition of the Ni, Co and Cu, which are austenite stabilization elements, would necessitate an addition of Cr and Mo in an increased amount for formation of a single-phase ferritic structure as required in the present invention.

Preferred content for each of the Ni, Co and Cu are as described below in view of the above-described reasons.

Ni: 0.05 to 5.0% by weight
Co: 0.05 to 5.0% by weight
Cu: 0.05 to 2.5% by weight

An alloy which meets the conditions described in (I) or (II) would have an improved workability as well as sufficient pitting resistance, weld zone-corrosion resistance (intergranular corrosion resistance) and acid resistance, and therefore, would be adequate for a variety of applications including automobile muffler, can body of a water heater, and chemical plant materials.

In the production of the Fe-Cr alloy of the present invention described in (I) or (II), a high-purity electrolytic iron, an electrolytic Cr, a metallic Mo, a metallic Ti, a metallic Nb, a metallic Zr, a metallic V, a metallic Ta, a metallic W, a high purity (Fe-B), an electrolytic Ni, an electrolytic Cu, and a metallic Co may be employed for the starting materials. The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting are carried out under an ultra-high vacuum of 10^{-7} torr or less for the production of the Fe-Cr alloy of the present invention.

(III) The Fe-Cr alloy of the present invention which has an improved workability as well as excellent pitting resistance, weld zone-corrosion resistance (intergranular corrosion resistance), and oxidation resistance is described below.

FIG. 27 diagrammatically shows results of oxidation resistance test (weight loss upon scale removal after exposure to air at 1,350 K for 12 hours) for a series of Fe-(15-30)% Cr alloy plates having a total content of C, N, O, P and S of up to 100 ppm. As apparent from FIG. 27, the alloy containing 0.1% or more of (3Al + 2Si + Mn) would have an improved oxidation resistance.

FIG. 28 diagrammatically shows results of oxidation resistance test (weight loss upon scale removal after exposure to air at 1,350 K for 12 hours) for a series of Fe-(15-30)% Cr alloy plates having a total content of C, N, O, P and S of up to 100 ppm. As apparent from FIG. 28, the alloy containing 0.001% or more of (4Ca + 4Mg + REM) would have an improved oxidation resistance.

The composition of the alloy according to this invention and aspects of the invention are described below. The Fe-Cr alloy of the present invention having an improved workability as well as an excellent oxidation resistance has three aspects as described below.

(1) First Aspect of the Invention

Cr: Cr content is limited to the range of from 5 to 60% by weight, and preferably, from 10 to 40% by weight. When the Cr content is within such a range and other conditions are also satisfied, the resulting alloy would have a sufficient oxidation resistance. Addition of the Cr in excess of such an amount is likely to induce a decrease in workability, and would not contribute to further improvement in the oxidation resistance.

C, N, O, P and S: These elements are contained in total content of 100 ppm or less, and preferably, 85 ppm or less. Abnormal oxidation is avoided when such conditions are satisfied. Such conditions in association with other conditions would result in an alloy having an improved oxidation resistance as well as an excellent ductility, and hence, high workability.

Mo: Mo content is limited to the range of from 0.5 to 20% by weight, and preferably, from 1 to 10% by weight. Mo added to an amount of 0.5% by weight or more will result in an improved pitting resistance, while an excessive addition of Mo is undesirable from economic point of view.

Ti, Nb, Zr, V, Ta, W and B: The alloy of the present invention contains at least one element selected from Ti, Nb, Zr, V, Ta, W and B in an amount that meets the following relation (1):

$$0.01 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt } \% \quad (1),$$

and preferably, in an amount that meets the following relation (1a):

$$0.05 \text{ wt } \% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 0.5 \text{ wt } \% \quad (1a).$$

The alloy of the present invention containing such elements in an amount within the range defined by such a relation has a significantly improved weld zone-corrosion resistance (intergranular corrosion resistance). However, an excessive addition of such elements is undesirable since a decrease in workability is likely to be induced by solid-solution strengthening of such elements themselves.

An Fe-Cr alloy which meets the above-described conditions would have a significantly improved workability as well as sufficient pitting resistance and weld zone-corrosion resistance (intergranular corrosion resistance), and therefore, would be adequate for a variety of applications including can body of a water heater and automobile muffler.

Si, Mn, Al: The alloy of the first aspect of the invention contains at least one such metal in an amount that meets the following relation (3):

$$0.1 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt } \% \quad (3),$$

and preferably, in an amount that meets the following relation (3a):

$$0.5 \text{ wt } \% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 25 \text{ wt } \% \quad (3a).$$

When the content is within such a range and other conditions are also satisfied, the resulting alloy would have a significantly improved oxidation resistance. These elements should not be contained in an excess amount since the elements contained such that the (3Al + 2Si + Mn) value is in excess of the range of relation (3) would render the alloy production difficult.

Preferably, the elements are respectively contained in the amounts as described below for the reasons as noted below.

Si: 0.1 to 10.0% by weight

Inclusion of less than 0.1% by weight is not significantly effective. Inclusion in excess of 10.0% by weight would result in a significantly decreased produceability.

Mn: 0.1 to 5.0% by weight

Inclusion of less than 0.1% by weight is not significantly effective. Inclusion in excess of 5% by weight would result in a significantly decreased produceability.

Al: 0.1 to 4.0% by weight

Inclusion of less than 0.1% by weight is not significantly effective. Inclusion in excess of 10.0% by weight would result in a significantly decreased produceability.

An Fe-Cr alloy which meets the above-described conditions would have an improved oxidation resistance as well as excellent workability, and therefore, such an alloy may be adequately used for producing various components in automobile exhaust gas system or various pipes used under the

conditions of repeated high-temperature oxidation.

(2) Second Aspect of the Invention

5 With regard to the Cr content, the content of C, N, O, P, and S, and the Fe content, what has been described for the alloy according to the first aspect of the invention applies to the alloy according to the second aspect of the invention.

The alloy according to the second aspect of the invention comprises at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (4):

$$10 \quad 0.001 \text{ wt } \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt } \% \quad (4),$$

and preferably, in an amount that meets the following relation (4a):

$$15 \quad 0.005 \text{ wt } \% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.15 \text{ wt } \% \quad (4a).$$

When the content is within such a range and other conditions are also satisfied, the resulting alloy would have a sufficient oxidation resistance as well as an excellent workability.

20 These elements are significantly effective in improving the protectability of the oxide film formed on the surface of the alloy according to the second aspect of the invention, and hence, in suppressing the abnormal oxidation which is likely to take place in an extremely thin material. The elements also improve adhesion of the oxide film to the underlying material.

An excessive inclusion of these elements to an amount such that the $(4\text{Ca} + 4\text{Mg} + \text{REM})$ value is in excess of 0.2% by weight is undesirable since such an addition is likely to result in surface defects of the resulting alloy.

25 Preferably, Ca, Mg and the rare earth metal are respectively contained in the amounts as described below for the reasons as noted below.

Ca: 0.002 to 0.01% by weight

30 Inclusion of less than 0.002% by weight is not significantly effective. Inclusion in excess of 0.01% by weight would result in a significantly decreased produceability.

Mg: 0.002 to 0.01% by weight

Inclusion of less than 0.002% by weight is not significantly effective. Inclusion in excess of 0.01% by weight would result in a significantly decreased produceability.

Rare earth metal: 0.005 to 0.1% by weight

35 Inclusion of less than 0.005% by weight is not significantly effective. Inclusion in excess of 0.1% by weight would result in an increased cost.

The alloy according to the second aspect of the invention may be used for applications similar to those of the alloy according to the first aspect of the invention.

40 (3) Third Aspect of the Invention

The alloy according to the third aspect of the invention comprises an alloy which meets the conditions for both the alloys according to the first and the second aspects of the invention, namely, an alloy having a Cr content of from 3 to 60% by weight; a total content of C, N, O, P and S of up to 100 ppm; a Mn content of from 0.5 to 20% by weight; a content of at least one member selected from Ti, Nb, Zr, V, Ta, W and B in the range that meets the above-mentioned relation (1); a content of at least one member selected from Si, Mn and Al in the range that meets the above-mentioned relation (2); and a content of at least one member selected from Ca, Mg, and rare earth metals (REM) in the range that meets the above-mentioned relation (3). Such an alloy has an excellent workability as well as an oxidation resistance even superior to that of the alloy according to the first or the second aspect of the invention, and therefore, may be appropriately used for any of the above-mentioned applications.

50 In the production of the Fe-Cr alloy of the present invention including the above-described three aspects, an ultra high-purity electrolytic iron, an electrolytic chromium, a zone melting-processed silicon, a molten salt-electrolytic manganese, a molten salt-electrolytic aluminum, a molten salt-electrolytic calcium, an electrolytically reduced magnesium, and an electrolytically reduced rare earth metal may be employed as the starting materials. The primary impurity is oxygen regardless of the type of the starting material, and therefore, melting and casting are carried out under an ultra-high vacuum of 10^{-5} torr or less for the production of the Fe-Cr alloy of the present invention.

(IV) The Fe-Cr alloy of the present invention which has an excellent acid resistance and oxidation resistance in addition to improved workability, pitting resistance and weld zone corrosion resistance is described below.

5 The alloy of this invention comprises the alloy of particularly excellent acid resistance described in the above (II) having added thereto the components of the alloy of particularly improved oxidation resistance described in the above (III). In view of such situation, the alloy of this invention is hereinafter described merely for its composition, and detailed description for each alloy component is omitted since it is the same as the one given in (II) and (III).

10 As in the case of (III), this invention, comprises three aspects. The content of C + N + O + P is up to 100 ppm; the Cr content is from 5 to 60% by weight; the Mo content is from 0.5 to 20% by weight; and the content of Ti + Nb + Zr + V + W + 50B is from 0.01 to 1% in all three aspects of the invention. The components which may vary are described below for each aspect.

15 (1) First Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (2):

20 $0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (2).$

The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (3):

25 $0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (3),$

and preferably, in an amount that meets the following relation:

30 $0.5 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 25 \text{ wt \%} \quad (3a).$

(2) Second Aspect of the Invention

The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (2):

35 $0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (2).$

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (4):

40 $0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (4),$

and preferably, in an amount that meets the following relation:

45 $0.005 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.15 \text{ wt \%} \quad (4a).$

(3) Third Aspect of the Invention

50 The alloy contains at least one member selected from Ni, Co and Cu in an amount that meets the following relation (2):

$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (2).$

55 The alloy also contains at least one member selected from Si, Mn and Al in an amount that meets the following relation (3):

$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (3),$

and preferably, in an amount that meets the following relation:

$$0.5 \text{ wt}\% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 25 \text{ wt}\% \quad (3a).$$

5

The alloy also contains at least one member selected from Ca, Mg and rare earth metals (REM) in an amount that meets the following relation (4):

$$0.001 \text{ wt}\% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt}\% \quad (4),$$

10

and preferably, in an amount that meets the following relation:

$$0.005 \text{ wt}\% \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.15 \text{ wt}\% \quad (4a).$$

15

The process for producing the alloy of this invention is the same as the above-described processes, and therefore, detailed description of the production process is omitted.

EXAMPLES

20

[A] Inventions of category A

The present invention is hereinafter described in further detail by referring to the Examples.

(Example 1) Alloys 1 to 13 of the invention and Comparative alloys 1 to 12 corresponding to Claim 1

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Alloys having the chemical compositions shown in Table 1 were prepared by melting and casting the materials in a 10 kg vacuum melting furnace, and the alloys were hot rolled into hot rolled plates of 4 mm thick. The plates were further subjected to recrystallization annealing, descaling, and cold rolling to produce cold rolled plates of 0.7 mm thick. Finally, the plates were subjected to a recrystallization annealing to produce annealed cold rolled plates.

30

The thus obtained annealed cold rolled plates were subjected to a tensile test according to JIS Z-2241 to evaluate for their elongation. The elongation is shown in Table 2. The plates were also subjected to a bend test by tightly folding to 180° in C direction after cold rolling to 50%. After the bend test, the plates were examined for cracks, and the thus examined conditions are shown in Table 2.

35

It should be noted that the elongation shown in Table 2 is an average of the elongation in L, X and C directions $((El_L + El_C + 2 \times El_X) / 4)$. The bend-working properties were evaluated in accordance with the following criteria:

- O: no crack,
- Δ: minute cracks, and
- X: large cracks.

40

The test samples obtained in all examples were evaluated for their increase in elongation and decrease in proof stress (yield strength).

The increase in elongation (%) and the decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm.

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The tensile properties used for such calculation are:

Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

50

elongation: 25%

proof stress: 450 N/mm²

By reducing the C, N, O, P and S, which have been well known impurities, to a total content of 100 ppm or less, the alloy plate would have an excellent workability irrespective of its Cr content as evidenced by the absence of cracks after 50% cold rolling and complete folding in C direction. On the other hand, minute cracks were observed, in the alloys of a relatively low Cr content when the total content was in excess of 100 ppm and up to 200 ppm, (Comparative alloys 1, 2, 3 and 4), and large cracks were observed in the alloys of a relatively low Cr content when the total content was in excess of 200 ppm, and in the alloys of a relatively high Cr content when the total content was in excess of 100 ppm (Comparative Alloys

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5, 6, 7, 8 and 9), indicating reduced workability.

In addition, comparison of the results among the alloys of equivalent Cr content reveals that the elongation is significantly improved by reducing the total content of the C, N, O, P and S to 100 ppm or less.

5 A series of alloys having the composition: Fe - 11% Cr- 0.003% Si - 0.005% Mn - 0.007% Al and varying total contents of C, N, O, P and S were prepared in the same manner as the alloy plates of Table 1, and ground finished with Emery #600. The alloy plates were then subjected to a salt spray test using 5% NaCl at 50 °C (24 hr), and examined for rust development. The results are shown in Table 2 (Criteria: A: no rust; B: little rust; C: considerable rust; and D: severe rust).

10 The above results reveal that the rust resistance is markedly improved to eventually show no rust when the total content of C, N, O, P and S is reduced to 100 ppm or less.

(Example 2) Alloys 14 to 20 of the invention and Comparative alloys 13 and 14 corresponding to Claim 2

15 Test materials having the chemical compositions shown in Table 1 were prepared in a 100 kg high-frequency induction heating ultra high-vacuum melting furnace. The test materials were forged, cut, hot rolled, annealed, and cold rolled to produce a steel plate of 1.0 mm thick.

Test samples of 1 mm (thickness) x 50 mm x 50 mm were prepared from the thus produced test materials. The test samples were then subjected to

20 (1) a test wherein the samples are immersed in 5% HCl at 40 °C for 24 hours; and

(2) a test wherein the samples are immersed in 40% H₂SO₄ at 50 °C for 24 hours

to measure the corrosion rate (g/m²•hr). The results are shown in Table 2. The results in Table 2 reveal that the corrosion upon immersion in an acid is markedly reduced in the samples having the alloy composition within the scope of the present invention compared to those of the comparative examples. With regard to 25 the samples having a total content of C, N, O, P and S of up to 100 ppm, the improvement is significant when Co + Ni + 2Cu is 0.01% or more.

As apparent from the results, the Fe-Cr based alloy (5 ≤ Cr ≤ 60) having a total content of C, N, O, P and S of up to 100 ppm and a content of at least one member selected from Cu, Ni and Co in the range of 0.01 wt % ≤ Ni + Co + 2Cu ≤ 6 wt% has an improved acid resistance.

30

(Example 3-1) Alloys 21 to 33 of the invention and Comparative alloys 15 to 18 corresponding to Claim 3

Test materials having the chemical compositions shown in Table 1 were prepared in a 100 kg high-frequency induction heating ultra-vacuum melting furnace. The thus prepared test materials were repeatedly 35 forged, cut, hot rolled, annealed, and cold rolled to produce a foil strip having a thickness of 50 μm and a width of 200 mm.

Test samples (50 μm (thickness) x 50 mm x 50 mm) were prepared from the above-described foil strips, and the test samples were subjected to a continuous oxidation test and a repeated heating test as described below. The results are shown in Table 2.

40

(1) Continuous oxidation test

The test strips were heated to 1,150 °C for 300 hours in the air, and then measured for their abnormally oxidized area. The results were evaluated in accordance with the following criteria:

45

O: no abnormally oxidized area;

O: up to 5% of the abnormally oxidized area;

Δ: 5 to 20% of the abnormally oxidized area;

X: 20 to 40% of the abnormally oxidized area; and

XX: more than 40% of the abnormally oxidized area.

50

(2) Repeated heating test

The test strips were subjected to 50 cycles of heating at 1,150 °C for 30 minutes and cooling for 30 minutes, and then measured for their area of the oxide film that had been peeled. The results were 55 evaluated in accordance with the following criteria:

O: no abnormally oxidized area;

O: up to 10% of the abnormally oxidized area;

Δ: 10 to 30% of the abnormally oxidized area;

X: 30 to 50% of the abnormally oxidized area; and

XX: more than 50% of the abnormally oxidized area.

Development of the abnormal oxidation was less significant in the test samples having the alloy composition within the scope of the present invention compared to that of the comparative examples. In addition, the oxide films of the test samples of the invention were free from defects and highly adhesive to the underlying material while those of the comparative examples were less adhesive to the underlying material and susceptible to abnormal oxidation. Furthermore, with regard to the test samples having the total content of C, P, O, N and S of up to 100 ppm, the improvements were significant when the $(3Al + 2Si + Mn)$ was 0.1% or more. As apparent from such results, a highly oxidation-resistant Fe-Cr alloy may be obtained by reducing the total content of S, P, O, N and C to 100 ppm or less, and adding at least one or two members selected from Si, Al and Mn to a content of 0.1% by weight $3Al + 2Si + Mn \leq 50\%$ by weight in the Fe-Cr based alloy ($3 \leq Cr \leq 60$).

The results also indicate that the oxidation resistance of the Fe-Cr alloy may be further improved by adding at least one member selected from Ca, Mg, and rare earth metals to a content of 0.001% by weight $\leq 4Ca + 4Mg + REM \leq 0.2\%$ by weight in addition to the above-mentioned elements.

(Example 3-2)

Alloys 34 to 41 of the invention and Comparative alloys 19 and 20 corresponding to Claim 3

Test materials having the chemical compositions shown in Table 1 were prepared in a 100 kg high-frequency induction heating ultra-vacuum melting furnace. The thus prepared test materials were repeatedly forged, cut, hot rolled, annealed, and cold rolled to produce a foil strip having a thickness of 50 μm and a width of 200 mm.

Foil strip test samples (50 μm (thickness) x 50 mm x 50 mm) were prepared from the above-described foil strips, and the test samples were subjected to a continuous oxidation test and a repeated heating test as in the case of Example 3-1 except that the heating temperature is 1100 °C. The results are shown in Table 2.

In the tests, the results were evaluated in accordance with the following criteria:

(1) Continuous oxidation test

O: up to 5% of the abnormally oxidized area;

Δ : 5 to 20% of the abnormally oxidized area;

X: more than 20% of the abnormally oxidized area.

(2) Repeated heating test

O: up to 10% of the abnormally oxidized area;

Δ : 10 to 30% of the abnormally oxidized area;

X: more than 30% of the abnormally oxidized area.

Development of the abnormal oxidation was less significant in the test samples having the alloy composition within the scope of the present invention compared to that of the comparative examples. In addition, the oxide films of the test samples of the invention were free from defects and highly adhesive to the underlying material while those of the comparative examples were less adhesive to the underlying material and susceptible to abnormal oxidation.

As apparent from such results, a highly oxidation-resistant Fe-Cr alloy may be obtained by reducing the total content of the S, P, O, N and C to 100 ppm or less, and adding at least one member selected from Ca, Mg, and rare earth metals to the content of 0.001 $\leq 4Ca + 4Mg + REM \leq 0.2$ in the Fe-Cr based alloy ($3 \leq Cr \leq 60$).

(Example 4) Alloys 42 to 44 of the invention and Comparative alloy 21 corresponding to Claim 4

Test materials having the chemical compositions shown in Table 1 were prepared in a 100 kg high-frequency induction heating ultra-vacuum melting furnace. The thus prepared test materials were repeatedly forged, cut, hot rolled, annealed, and cold rolled to produce a foil strip having a thickness of 50 μm and a width of 200 mm.

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The thus prepared test samples were then subjected to (1) a corrosion test wherein the samples are immersed in 5% HCl at 40 °C; (2) a corrosion test wherein the samples are immersed in 40% H₂SO₄ at 50 °C; (3) a continuous oxidation test; and (4) a repeated heating test by repeating the procedure of the above-described examples. The results were also evaluated in a similar manner. The results are shown in Table 2. The results clearly reveal that the test samples having the alloy composition within the scope of the present invention have excellent properties.

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Table 1 (1)

	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements	α'	β	γ	δ
1	7	10	14	21	13	3.9		0.001	0.001	0.001		65	-	-	-
2	31	6	25	8	7	11.4		0.001	0.001	0.001		77	-	-	-
3	10	20	30	5	14	7.3		0.0004	0.008	0.024		79	-	-	-
4	16	9	10	24	8	15.7		0.011	0.020	0.001		67	-	-	-
5	8	8	10	6	6	20.8		0.001	0.006	0.017		38	-	-	-
6	4	4	8	4	6	16.2		0.0003	0.031	0.016		26	-	-	-
7	15	6	12	8	10	18.4		0.002	0.005	0.002		51	-	-	-
8	10	26	10	10	35	36.1		0.001	0.010	0.032		91	-	-	-
9	5	35	10	8	7	58.8		0.009	0.014	0.008		55	-	-	-
10	15	10	25	14	10	11.0		0.007	0.003	0.005		74	-	-	-
11	4	10	5	7	18	11.0		0.007	0.003	0.005		44	-	-	-
12	15	35	20	10	5	11.0		0.007	0.003	0.005		85	-	-	-
13	20	15	5	25	6	11.0		0.007	0.003	0.005		71	-	-	-

Unit: wt%, *: ppm

 $\alpha = \text{C+N+O+S+P}$, $\beta = \text{Ni+Co+2Cu}$, $\gamma = 3\text{Al}+2\text{Si}+\text{Mn}$, $\delta = 4\text{Ca}+4\text{Mg}+\text{REM}$

Table 1 (2)

Alloys of invention															
	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements	α^*	β	γ	δ
14	21	22	20	14	10	19	0.06	0.002	0.01	0.01	Ni:0.60	87	0.60	-	-
15	18	17	30	16	9	52	0.07	0.002	0.02	0.01	Co:0.01	90	0.01	-	-
16	30	14	25	10	11	11	0.05	0.001	0.02	0.02	Cu:1.5	90	3.0	-	-
17	26	13	31	12	8	36	0.04	0.001	0.01	0.01	Ni:4, Co:2	90	6.0	-	-
18	16	20	27	17	14	6.5	0.03	0.002	0.03	0.01	Ni:0.5, Co:1.4, Cu:0.5	94	2.9	-	-
19	13	10	16	15	9	5.9	0.01	0.001	0.01	0.01	Ni:3.0	63	3.0	-	-
20	9	13	18	10	15	18	0.02	0.002	0.01	0.01	Ni:0.11	65	0.11	-	-
21	11	30	20	11	11	24	0.01	0.02	0.06	0.03		83	-	0.21	-
22	16	26	22	10	9	11.5	0.02	0.02	0.05	0.15		83	-	0.31	-
23	23	20	26	12	10	36	0.01	0.04	0.06	0.04		91	-	0.28	-
24	13	24	20	13	10	56	0.01	16.0	0.05	0.03		80	-	48.13	-
25	15	30	21	16	13	3.5	0.03	0.03	18	5		95	-	41.09	-
26	9	13	21	15	10	17.0	0.01	1.20	0.53	0.20		68	-	4.86	-

Unit: wt%, *: ppm

 $\alpha = \text{C+N+O+S+P}$, $\beta = \text{Ni+Co+2Cu}$, $\gamma = 3\text{Al}+2\text{Si+Mn}$, $\delta = 4\text{Ca}+4\text{Mg+REM}$

Table 1 (3)

Alloys of invention														
C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements	α^*	β	γ	δ
27	15	21	16	10	9	15.9	0.02	2.61	0.23	1.11	71	-	9.40	-
28	21	24	24	10	12	13.0	0.02	0.001	0.02	Ca:0.001	91	-	0.063	0.004
29	16	32	22	11	14	26	0.02	16.0	0.40	Mg:0.0003	95	-	50.8	0.0012
30	18	20	24	13	17	31	0.01	5.0	0.07	REM:0.0015	92	-	15.24	0.0015
31	14	30	23	11	10	40	0.03	1.0	0.6	Ca:0.0005, Mg:0.0008	88	-	4.23	0.0052
32	15	21	33	14	11	18	0.02	0.1	0.5	Ca:0.001, Mg:0.001, REM:0.01	94	-	1.8	0.018
33	11	23	15	10	19	6.8	0.01	0.08	0.2	Ca:0.001	78	-	0.7	0.004
34	13	26	21	10	12	3.5	0.01	0.002	0.01	Ca:0.008	82	-	0.036	0.032
35	14	20	23	11	9	17	0.01	0.001	0.02	Mg:0.05	77	-	0.053	0.20
36	18	23	24	18	13	31	0.005	0.001	0.02	REM:0.001	96	-	0.043	0.001
37	12	24	20	13	8	26	0.01	0.002	0.01	Ca:0.0005, REM:0.002	77	-	0.036	0.004
38	15	20	26	15	16	57	0.01	0.003	0.01	Ca:0.0002, Mg:0.0002, REM:0.0005	92	-	0.039	0.0021
39	9	21	28	10	9	7.5	0.01	0.001	0.01	Mg:0.01	77	-	0.033	0.04

Unit: wt%, *: ppm

 $\alpha = C+N+O+S+P$, $\beta = Ni+Co+2Cu$, $\gamma = 3Al+2Si+Mn$, $\delta = 4Ca+4Mg+REM$

Table 1 (4)

Alloys of invention											
	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements
40	20	16	10	10	9	18	0.01	0.001	0.01	0.01	Ca:0.006
41	10	18	17	13	11	21	0.01	0.001	0.02	0.01	REM:0.001, Mg:0.003
42	13	14	31	10	9	7.0	0.01	1.0	0.5	0.03	Ni:0.6, Co:1.4, Cu:0.5, Ca:0.001, Mg:0.001, REM:0.001
43	9	18	22	10	10	13.0	0.01	0.002	0.001	0.003	Ni:0.5, Co:1.0, Cu:0.8, Ca:0.005, Mg:0.005, REM:0.002
44	7	21	26	10	10	15.9	0.01	0.5	1.2	0.90	Ni:0.3, Co:0.6, Cu:1.0, Ca:0.002

Unit: wt%, *: ppm

 $\alpha = \text{C+N+O+S+P}$, $\beta = \text{Ni+Co+2Cu}$, $\gamma = 3\text{Al}+2\text{Si}+\text{Mn}$, $\delta = 4\text{Ca}+4\text{Mg}+\text{REM}$

Table 1 (5)

	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements	α^*	β	γ	δ
1	81	8	10	21	12	0.85		0.001	0.001	0.001		132	-	-	-
2	8	20	15	9	52	11.3		0.001	0.001	0.001		104	-	-	-
3	21	15	8	75	8	7.3		0.001	0.001	0.001		127	-	-	-
4	12	12	88	20	11	11.3		0.001	0.001	0.001		143	-	-	-
5	32	72	40	80	30	11.5		0.001	0.001	0.001		254	-	-	-
6	35	20	38	105	10	16.3		0.0003	0.031	0.016		209	-	-	-
7	45	40	30	220	15	20.8		0.001	0.006	0.018		350	-	-	-
8	18	58	28	32	10	36.0		0.002	0.005	0.020		146	-	-	-
9	61	56	18	9	15	59.1		0.003	0.011	0.015		159	-	-	-
10	18	25	30	15	25	11.0		0.007	0.003	0.005		113	-	-	-
11	40	58	45	20	31	11.0		0.007	0.003	0.005		194	-	-	-
12	50	65	35	82	30	11.0		0.007	0.003	0.005		262	-	-	-
Comparative alloys															

Unit: wt%, *: ppm

 $\alpha = C+N+O+S+P$, $\beta = Ni+Co+2Cu$, $\gamma = 3Al+2Si+Mn$, $\delta = 4Ca+4Mg+REM$

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Table 2 (1)

	Alloys of invention									
	Increase in elongation (%)	Decrease in proof stress (N/mm ²)	Elongation (%)	Bend workability	Salt spray test	Corrosion rate in g/m ² ·hr upon immersion in 5% HCl, 40°C	Corrosion rate in g/m ² ·hr upon immersion in 40% H ₂ SO ₄ , 50°C	Continuous oxidation test	Repeated heating test	
1	+ 7.1	- 106	46	○	-	—	—	—	—	
2	+ 6.9	- 103	41	○	-	—	—	—	—	
3	+ 5.3	- 103	43	○	-	—	—	—	—	
4	+ 7.1	- 109	39	○	-	—	—	—	—	
5	+ 10.0	- 125	35	○	-	—	—	—	—	
6	+ 9.8	- 131	37	○	-	—	—	—	—	
7	+ 9.5	- 118	38	○	-	—	—	—	—	
8	+ 5.9	- 93	29	○	-	—	—	—	—	
9	+ 8.2	- 116	21	○	-	—	—	—	—	
10	+ 6.8	- 103	-	-	Λ	—	—	—	—	
11	+ 10.1	- 129	-	-	Λ	—	—	—	—	
12	+ 5.6	- 98	-	-	Λ	—	—	—	—	
13	+ 5.9	- 103	-	-	Λ	—	—	—	—	
14	+ 5.8	- 87	-	-	-	0.55	13.0	—	—	
15	+ 6.1	- 95	-	-	-	0.40	7.6	—	—	

Table 2 (2)

	Alloys of invention									
	Increase in elongation (%)	Decrease in proof stress (N/mm ²)	Elongation (%)	Bend workability	Salt spray test	Corrosion rate in g/m ² .hr upon immersion in 5% HCl, 40°C	Corrosion rate in g/m ² .hr upon immersion in 40% H ₂ SO ₄ , 50°C	Continuous oxidation test	Repeated heating test	
16	+ 5. 5	- 8 6	-	-	-	1. 2	21. 8	-	-	
17	+ 5. 6	- 9 0	-	-	-	0. 3 8	8. 8	-	-	
18	+ 5. 3	- 8 5	-	-	-	2. 8	39. 2	-	-	
19	+ 6. 5	- 108	-	-	-	3. 1	56. 3	-	-	
20	+ 7. 3	- 111	-	-	-	1. 6	29. 6	-	-	
21	+ 5. 4	- 8 9	-	-	-	—	—	○	○	
22	+ 5. 6	- 8 9	-	-	-	—	—	○	○	
23	+ 6. 3	- 8 8	-	-	-	—	—	○	○	
24	+ 9. 2	- 103	-	-	-	—	—	⊙	⊙	
25	+ 5. 6	- 9 6	-	-	-	—	—	○	⊙	
26	+ 6. 3	- 9 5	-	-	-	—	—	○	○	
27	+ 6. 3	- 9 0	-	-	-	—	—	⊙	⊙	
28	+ 5. 5	- 8 3	-	-	-	—	—	○	⊙	
29	+ 6. 1	- 9 0	-	-	-	—	—	○	⊙	
30	+ 6. 1	- 8 9	-	-	-	—	—	⊙	⊙	

Table 2 (3)

	Increase in elongation (%)	Decrease in proofstress (N/mm ²)	Elongation (%)	Hard-ability	Salt spray test	Corrosion rate in g/m ² ·hr upon immersion in 5% HCl, 40°C	Corrosion rate in g/m ² ·hr upon immersion in 40% H ₂ SO ₄ , 50°C	Continuous oxidation test	Repeated heating test
31	+ 6.1	- 93	-	-	-	—	—	⊙	⊙
32	+ 6.8	- 89	-	-	-	—	—	⊙	⊙
33	+ 7.0	- 95	-	-	-	—	—	○	○
34	+ 6.5	- 99	-	-	-	—	—	○	△
35	+ 7.1	- 98	-	-	-	—	—	○	○
36	+ 6.0	- 90	-	-	-	—	—	○	○
37	+ 7.5	- 108	-	-	-	—	—	○	⊙
38	+ 7.8	- 96	-	-	-	—	—	○	⊙
39	+ 7.1	- 93	-	-	-	—	—	○	○
40	+ 7.3	- 110	-	-	-	—	—	○	○
41	+ 7.5	- 106	-	-	-	—	—	○	⊙
42	+ 6.5	- 105	-	-	-	3.0	42.6	○	○
43	+ 7.4	- 107	-	-	-	1.1	20.9	○	⊙
44	+ 7.3	- 100	-	-	-	0.71	15.0	⊙	⊙

Alloys of invention

table 2 (4)

	Increase in elongation (%)	Decrease in proofstress (N/mm ²)	Elongation (%)	Bend workability	Salt spray test	Corrosion rate in g/m ² ·hr upon immersion in 5% HCl, 40°C	Corrosion rate in g/m ² ·hr upon immersion in 40% H ₂ SO ₄ , 50°C	Continuous oxidation test	Repeated heating test
1	+ 3.8	- 55	38	Δ	-	—	—	—	—
2	+ 4.8	- 75	36	Δ	-	—	—	—	—
3	+ 3.7	- 63	38	Δ	-	—	—	—	—
4	+ 3.3	- 60	33	Δ	-	—	—	—	—
5	+ 1.7	- 31	30	X	-	—	—	—	—
6	+ 2.0	- 40	30	X	-	—	—	—	—
7	+ 1.0	- 17	28	X	-	—	—	—	—
8	+ 3.2	- 56	23	X	-	—	—	—	—
9	+ 2.9	- 48	15	X	-	—	—	—	—
10	+ 4.7	- 78	-	-	B	—	—	—	—
11	+ 2.6	- 45	-	-	C	—	—	—	—
12	+ 1.6	- 28	-	-	D	—	—	—	—
13	+ 3.6	- 60	-	-	-	12.2	364	—	—
14	+ 4.1	- 63	-	-	-	13.5	408	—	—
15	+ 4.1	- 55	-	-	-	—	—	X	X

Comparative alloys

Table 2 (5)

	Increase in elongation (%)	Decrease in proof stress (N/mm ²)	Elongation (%)	Bend workability	Salt spray test	Corrosion rate in g/m ² .hr upon immersion in 5% HCl, 40°C	Corrosion rate in g/m ² .hr upon immersion in 40% H ₂ SO ₄ , 50°C	Continuous oxidation test	Repeated heating test
Comparative alloys	16 + 2.8	- 5.5	-	-	-	—	—	XX	XX
	17 + 3.5	- 5.5	-	-	-	—	—	X	X
	18 + 3.3	- 5.8	-	-	-	—	—	Δ	X
	19 + 3.5	- 5.6	-	-	-	—	—	Δ	Δ
	20 + 2.0	- 3.5	-	-	-	—	—	Δ	X
	21 + 4.0	- 7.0	-	-	-	0.9	18.3	O	X

55 Industrial Utility

Fe-Cr alloys of improved workability having excellent acid resistance and/or oxidation resistance are provided. Such Fe-Cr alloys may be utilized in a wide variety of fields.

[B] Inventions of category B

The present invention is hereinafter described in further detail by referring to the Examples.

5 (Example 1) Alloys 1 to 6 of the invention and Comparative alloys 1 to 6 corresponding to Claim 5

Alloys having the chemical compositions shown in Table 1 were prepared in an ultra high-vacuum melting furnace of 10^{-5} Torr or less from an ultra high-purity electrolytic iron and other high-purity metal materials produced, for example, by an electrolytic process.

10 The alloy materials were heated to about $1,200^{\circ}\text{C}$ and hot rolled into plates of about 5 mm thick, and finally, cold rolled to a thickness of 1.0 to 2.0 mm. The plates were further annealed at 500 to $1,100^{\circ}\text{C}$ for recrystallization and particle size adjustment.

Test samples were cut out of the thus prepared alloy materials for tensile tests at room temperature and at an elevated temperature in accordance with Japanese Industrial Standard (The tensile test at room temperature was carried out in accordance with JIS 5, and the tensile test at an elevated temperature was carried out in accordance with JIS G 0567).

The alloy materials of the Table 1 prepared in an ultra high-vacuum furnace from high-purity metals were also subjected to an oxidation test wherein the alloy materials were heated in an electric furnace open to atmosphere to 1,350 K for 12 hours, and cooled by air to room temperature, and measured for their weight loss after scale removal. The thus evaluated weight loss was used as an index for their oxidation resistance. The results are shown in Table 2. The results in Table 2 reveal that both the workability and the high-temperature strength are markedly improved in the samples having the alloy composition within the scope of the present invention compared to those of the comparative examples.

25 (Example 2) Alloys 7 to 12 of the invention and Comparative alloys 7 to 9 corresponding to Claim 6

Test materials having the chemical compositions shown in Table 1 were prepared in a 100 kg high-frequency induction heating ultra high-vacuum melting furnace. The test materials were forged, cut, hot rolled, annealed, and cold rolled to produce a steel plate of 1.0 mm thick.

30 Test samples of 1 mm (thickness) x 50 mm x 50 mm were prepared from the thus produced test materials. The test samples were then subjected to

(1) a test wherein the samples are immersed in 5% HCl at 40°C for 24 hours; and

(2) a test wherein the samples are immersed in 40% H_2SO_4 at 50°C for 24 hours

to measure the corrosion rate ($\text{g}/\text{m}^2\cdot\text{hr}$). The results are shown in Table 2. The results in Table 2 reveal that the corrosion upon immersion in an acid is markedly reduced in the samples having the alloy composition within the scope of the present invention compared to those of the comparative examples.

As apparent from the results, the Fe-Cr based alloy ($5 \leq \text{Cr} \leq 60$) having a total content of C, N, O, P and S of up to 100 ppm and a content of at least one member selected from Cu, Ni and Co in the range of $0.01 \text{ wt}\% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt}\%$ has an improved acid resistance.

40 In addition, as apparent from the results, the alloy further comprising at least one member selected from Ti, Nb, Zr, V, Ta, W and B in a content in the range of $0.01 \text{ wt}\% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6.0 \text{ wt}\%$ has a further improved acid resistance.

(Example 3) Alloys 13 to 26 of the invention and Comparative alloys 10 to 12 corresponding to Claim 7

45 Alloys having the chemical compositions shown in Table 1 were prepared in an ultra high-vacuum melting furnace of 10^{-7} Torr or less from an ultra high-purity electrolytic iron, an electrolytic Cr and other high-purity metal materials.

The alloy materials were heated to about $1,200^{\circ}\text{C}$ and hot rolled into plates of about 5 mm thick, and finally, cold rolled to a thickness of 1.0 to 2.0 mm. The plates were further annealed at 500 to $1,100^{\circ}\text{C}$ for recrystallization and particle size adjustment.

Test samples were cut out of the thus prepared alloy materials for tensile tests at room temperature and at an elevated temperature in accordance with Japanese Industrial Standard (The tensile test at room temperature was carried out in accordance with JIS 5, and the tensile test at an elevated temperature was carried out in accordance with JIS G 0567 at 900°C).

55 The samples were also subjected to an oxidation test wherein the samples were heated in an electric furnace open to atmosphere to 1,350 K for 12 hours, and cooled by air to room temperature, and measured for their weight loss after scale removal. The thus evaluated weight loss was used as an index for their

oxidation resistance. The test results are shown in Table 2. The results in Table 2 reveal that the oxidation resistance is markedly improved in the samples having the alloy composition within the scope of the present invention compared to those of the comparative examples.

5 (Example 4) Alloys 27 to 29 of the invention corresponding to Claim 8

Alloys having the chemical compositions shown in Table 1 were prepared in an ultra high-vacuum melting furnace of 10^{-7} Torr or less from an ultra high-purity electrolytic iron, an electrolytic Cr and other high-purity metal materials.

10 The alloy materials were heated to about 1,200 °C and hot rolled into plates of about 5 mm thick, and finally, cold rolled to a thickness of 1.0 to 2.0 mm. The plates were further annealed at 500 to 1,100 °C for recrystallization and particle size adjustment.

The thus prepared test samples were then subjected to (1) a corrosion test wherein the samples are immersed in 5% HCl at 40 °C; (2) a corrosion test wherein the samples are immersed in 40% H₂SO₄ at 50 °C; and (3) a high-temperature tensile test at 900 °C by repeating the procedure of the above-described examples.

15 The results were also evaluated in a similar manner. The results are shown in Table 2. The results clearly reveal that the test samples having the alloy composition within the scope of the present invention have excellent properties.

20 (Increase in elongation and decrease in proof stress)

The test samples obtained in all of the above-described examples were evaluated for their increase in elongation and decrease in proof stress (yield strength). The increase in elongation (%) and the decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm.

The tensile properties used for such calculation are:

Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

30 proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

elongation: 25%

proof stress: 450 N/mm²

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40

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Table 1 (1)

Alloys of invention	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn
1	15	11	5	30	5	18.6	0.03	0.003	0.02	0.02
2	20	10	10	39	15	20.3	0.08	0.002	0.01	0.01
3	25	15	15	20	17	13.7	0.05	0.004	0.01	0.02
4	30	10	10	30	15	4.2	0.04	0.011	0.02	0.02
5	35	11	9	30	10	45.2	0.07	0.005	0.02	0.03
6	25	12	7	35	15	14.5	0.06	0.02	0.01	0.02
7	21	11	36	11	14	18	0.05	0.001	0.02	0.02
8	10	20	22	18	12	22	0.07	0.002	0.02	0.01
9	18	15	30	14	15	30	0.03	0.001	0.02	0.01
10	25	10	29	15	9	8.7	0.06	0.002	0.03	0.02
11	29	18	19	10	16	54	0.06	0.002	0.04	0.01
12	16	10	31	10	9	5.3	0.01	0.001	0.01	0.02
13	20	10	10	40	10	13.5	0.08	0.12	0.01	—
14	20	10	10	40	5	13.3	0.05	0.03	2.3	6.3
15	18	21	16	19	15	18.0	0.03	2.31	0.08	0.02

Unit: wt%, *: ppm

Table 1 (2)

Alloys of Invention	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn
1 6	15	10	10	35	5	13.8	0.08	0.03	0.02	0.03
1 7	15	10	10	40	5	12.9	0.07	5.11	0.05	0.1
1 8	15	11	5	30	5	18.6	0.03	0.003	0.02	0.02
1 9	20	10	10	39	15	20.3	0.08	0.002	0.01	0.01
2 0	25	15	15	20	17	13.7	0.05	0.004	0.01	0.02
2 1	10	12	23	11	15	10.1	0.02	2.33	0.20	0.11
2 2	7	12	18	10	9	16.0	0.02	0.01	0.01	0.01
2 3	10	18	31	10	10	22.1	0.01	0.02	0.01	0.01
2 4	11	22	26	10	8	18.3	0.01	0.01	0.01	0.01
2 5	9	18	40	12	8	15.4	0.01	0.01	0.01	0.01
2 6	13	9	26	10	10	20.0	0.02	0.01	0.01	0.01
2 7	10	30	18	15	9	16.5	0.05	0.31	0.51	0.30
2 8	8	26	31	10	15	23.0	0.04	0.26	0.80	0.28
2 9	10	23	19	21	10	18.1	0.06	0.19	0.32	0.30

Unit: wt%, *: ppm

Table 1 (3)

com- parative alloys	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn
1	41	31	22	41	22	18.3	0.04	0.02	0.01	0.02
2	62	52	21	42	31	16.5	0.05	0.03	0.02	0.02
3	4	11	52	101	55	19.4	0.04	0.04	0.02	0.03
4	50	100	65	120	52	10.6	0.04	0.03	0.03	0.02
5	60	120	40	110	53	6.1	0.05	0.02	0.05	0.02
6	20	150	44	140	55	2.2	0.03	0.05	0.06	0.03
7	33	31	20	27	13	48	0.02	0.001	0.01	0.01
8	51	22	20	20	18	30	0.01	0.002	0.01	0.01
9	16	26	21	18	11	18	0.01	0.001	0.01	0.01
10	35	100	65	12	52	10.6	0.04	0.03	0.03	0.02
11	36	120	40	11	53	6.1	0.05	0.02	0.05	0.02
12	32	150	44	14	55	2.2	0.03	0.05	0.06	0.03

Unit: wt%, *: ppm

Table 1 (4)

Alloys of invention	Ti, Nb, Zr, V, Ta, W, B	Other elements	α^*	β	γ	δ	ε
1	Ti 0.03, Nb 0.03		66	0.06	—	—	—
2	Ta 0.01, W 0.5, Zr:0.01, B 0.0003		94	0.535	—	—	—
3	Ti 0.1, Zr 0.05, W 3.5 V 0.2, Ta 0.05, Nb 0.5		92	4.4	—	—	—
4	W 1, Zr 0.03, Ti 0.03		95	1.06	—	—	—
5	Ta 0.1, B 0.0005		95	0.125	—	—	—
6	Ta 0.01, Ti 0.01 B 0.0007		94	0.055	—	—	—
7	Ti 0.20	Ni 1.5	93	0.20	1.5	—	—
8	Nb 0.01	Co 3.0	82	0.01	3.0	—	—
9	Zr 0.30, V 0.05, B 0.005	Ni 2.2, Co 0.8	92	0.45	3.0	—	—
10	Ti 0.2, Ta 0.05, W 0.1	Ni 0.02, Cu 0.05	88	0.35	0.12	—	—

Unit: wt%, *: ppm

$\alpha = \text{C+N+O+P+S}$, $\beta = \text{Ti+Nb+Zr+V+Ta+W+50B}$,
 $\gamma = \text{Ni+Co+2Cu}$, $\delta = 3\text{Al}+2\text{Si}+\text{Mn}$,
 $\varepsilon = 4\text{Ca}+4\text{Mg}+\text{REM}$

Table 1 (5)

Alloys of invention	Ti, Nb, Zr, V, Ta, W, B	Other elements	α^*	β	γ	δ	ϵ
1 1	Nb 0.5, V 0.2, B 0.001	Ni 0.5, Cu 0.5, Co 2.0	92	0.72	3.5	—	—
1 2	Ti 0.11	Cu 0.4	76	0.11	0.8	—	—
1 3	Nb 0.5, B 0.0003, Zr 0.05, W 1.5		90	2.2	—	0.38	—
1 4	Nb 0.5, Zr 0.01, Ta 0.1, W 2.0		85	2.61	—	10.99	—
1 5	Ti 0.05, B 0.0005, W 2.0		89	2.075	—	7.11	—
1 6	W 3.5	REM 0.03, Ca 0.0010	75	3.5	—	0.16	0.034
1 7	V 0.2	Mg 0.0015, REM 0.01	80	0.2	—	15.33	0.016
1 8	Ti 0.07	REM 0.03	66	0.07	—	0.609	0.03
1 9	Ta 0.01, W 0.5, Zr 0.01, B 0.0003	Ca 0.0020	94	0.535	—	0.306	0.008
2 0	Ti 0.1, Zr 0.05, W 3.5, V 0.2, Ta 0.05, Nb 0.5	Ca 0.0010	92	4.4	—	0.412	0.004

Unit: wt%, *: ppm

$\alpha = \text{C+N+O+P+S}$, $\beta = \text{Ti+Nb+Zr+V+Ta+W+50B}$,
 $\gamma = \text{Ni+Co+2Cu}$, $\delta = 3\text{Al}+2\text{Si}+\text{Mn}$,
 $\epsilon = 4\text{Ca}+4\text{Mg}+\text{REM}$

Table 1 (6)

Alloys of Invention	Ti, Nb, Zr, V, Ta, W, B	Other elements	α^*	β	γ	δ	ε
2 1	Ti 0.5, W 2	Mg 0.0020, REM 0.0005	71	2.05	—	7.5	0.0025
2 2	Nb 0.31, Ti 0.14, W 0.1	Ca 0.005	56	0.55	—	0.06	0.02
2 3	Nb 0.26, Ti 0.22	Mg 0.002	79	0.48	—	0.09	0.008
2 4	Nb 0.51, Ti 0.33, Zr 0.05	REM 0.06	77	0.89	—	0.06	0.06
2 5	V 0.36, Ta 0.18	Ca 0.010, Mg 0.015, REM 0.04	87	0.54	—	0.06	0.14
2 6	W 0.5, B 0.0010	Ca 0.005, Mg 0.015	68	0.55	—	0.06	0.08
2 7	W 0.2, Nb 0.53	Ni 1.1, Co 0.6, Ca 0.006	82	0.73	1.7	2.25	0.024
2 8	Nb 0.36, Ti 0.18, Zr 0.38, V 0.16, B 0.0010	Ni 1.6, Co 0.8, Cu 0.03, Ca 0.006, Mg 0.001	90	1.13	2.46	2.66	0.028
2 9	Ti 0.16, V 0.32, Ta 0.19	Ni 1.5, Ca 0.003, Mg 0.005, REM 0.004	83	0.67	0.5	1.51	0.036

Unit: wt%, *: ppm

α = C+N+O+P+S, β = Ti+Nb+Zr+V+Ta+W+50B,
 γ = Ni+Co+2Cu, δ = 3Al+2Si+Mn
 ε = 4Ca+4Mg+REM

Table 1 (7)

Com- parative alloys	Ti, Nb, Zr, V, Ta, W, B	Other elements	α^*	β	γ	δ	ε
1			157	-	-	-	-
2	Ti 0.006, Nb 0.004		208	0.01	-	-	-
3			223	-	-	-	-
4			387	-	-	-	-
5			383	-	-	-	-
6			409	-	-	-	-
7	Nb 0.4, Zr 0.4, B 0.0005	Cu 8.5	124	0.81	17.0	-	-
8	Zr 0.004, W 0.002	Ni 0.005, Co 0.002	131	0.006	0.007	-	-
9	Ti 0.008	Co 0.005	92	0.008	0.005	-	-
10			264	-	-	0.17	-
11			260	-	-	0.18	-
12			295	-	-	0.3	-

Unit: wt%, *: ppm

α = C+N+O+P+S, β = Ti+Nb+Zr+V+Ta+W+50B,
 γ = Ni+Co+2Cu, δ = 3Al+2Si+Mn
 ε = 4Ca+4Mg+REM

Table 2 (1)

	Increase in elongation (%)	Decrease in yield strength N/mm ²	Elongation %	Yield strength N/mm ²	High temperature resistance N/mm ²	Weight loss in oxidation g/cm ² .12hr	Corrosion rate in g/m ² .hr upon immersion in 5N HCl, 40°C	Corrosion rate in g/m ² .hr upon immersion in 40% H ₂ SO ₄ , 50°C
1	+8.1	-115	37.2	218	20.4	9.8×10^{-4}	-	-
2	+6.0	-93	35.7	235	22.7	7.6×10^{-4}	-	-
3	+5.8	-95	34.3	247	29.5	9.1×10^{-4}	-	-
4	+6.4	-94	42.7	182	24.8	7.8×10^{-3}	-	-
5	+6.9	-102	24.4	363	22.8	2.3×10^{-4}	-	-
6	+6.4	-96	36.1	224	20.3	1.3×10^{-3}	-	-
7	+6.1	-95	-	-	21.3	-	0.81	13.9
8	+6.7	-100	-	-	18.1	-	0.70	9.2
9	+5.8	-95	-	-	21.5	-	0.61	8.5
10	+6.0	-103	-	-	22.3	-	2.6	44.4
11	+6.6	-91	-	-	24.6	-	0.30	6.6
12	+6.0	-98	-	-	20.4	-	2.0	20.3
13	+6.1	-93	-	-	25.1	$< 5 \times 10^{-3}$	-	-
14	+6.8	-100	-	-	26.3	$< 5 \times 10^{-3}$	-	-
15	+7.1	-89	-	-	26.3	$< 5 \times 10^{-3}$	-	-

Alloys of invention

Table 2 (2)

Alloys of invention								
	Increase in elongation (%)	Decrease in yield strength N/mm ²	Elongation %	Yield strength N/mm ²	High temperature resistance N/mm ²	Weight loss in oxidation g/cm ² .12hr	Corrosion rate in q/m ² .hr upon immersion in 5% HCl, 40°C	Corrosion rate in q/m ² .hr upon immersion in 40% H ₂ SO ₄ , 50°C
16	+7.3	-109	-	-	30.5	<5 × 10 ⁻³	-	-
17	+6.6	-102	-	-	20.3	<5 × 10 ⁻³	-	-
18	+8.1	-110	-	-	20.3	<5 × 10 ⁻³	-	-
19	+5.9	-96	-	-	22.0	<5 × 10 ⁻³	-	-
20	+6.0	-100	-	-	30.0	<5 × 10 ⁻³	-	-
21	+7.3	-105	-	-	26.8	<5 × 10 ⁻³	-	-
22	+9.6	-126	-	-	24.3	9.0 × 10 ⁻³	-	-
23	+6.3	-100	-	-	22.3	7.3 × 10 ⁻³	-	-
24	+6.9	-106	-	-	25.6	4.9 × 10 ⁻³	-	-
25	+6.0	-96	-	-	24.0	5.6 × 10 ⁻³	-	-
26	+7.5	-108	-	-	27.5	6.0 × 10 ⁻³	-	-
27	+6.3	-110	-	-	25.0	4.1 × 10 ⁻³	0.80	14.1
28	+5.9	-87	-	-	25.7	4.0 × 10 ⁻³	0.65	9.0
29	+6.6	-96	-	-	22.3	4.2 × 10 ⁻³	0.85	15.0

Table 2 (3)

Comparative alloys								
	Increase in elongation (%)	Decrease in yield strength N/mm ²	Elongation %	Yield strength N/mm ²	High temperature resistance N/mm ²	Weight loss in oxidation g/cm ² .12hr	Corrosion rate in g/m ² .hr upon immersion in 5HCl, 40°C	Corrosion rate in g/m ² .hr upon immersion in 40H ₂ SO ₄ .50°C
1	+3.2	-55	31.3	280	17.5	1.2×10^{-3}	-	-
2	+1.6	-28	33.4	269	17.6	1.4×10^{-3}	-	-
3	+1.4	-27	30.2	288	17.1	6.8×10^{-4}	-	-
4	+1.8	-33	34.5	241	16.9	9.8×10^{-3}	-	-
5	+2.1	-35	36.1	224	17.3	1.9×10^{-2}	-	-
6	+2.1	-39	37.9	207	17.5	2.8×10^{-2}	-	-
7	could not be hot-rolled							
8	+2.9	-56	-	-	17.6	-	5.2	102
9	+7.3	-103	-	-	17.0	-	8.8	160
10	+1.6	-28	-	-	16.8	9.8×10^{-3}	-	-
11	+1.5	-25	-	-	17.0	2.5×10^{-2}	-	-
12	+1.8	-24	-	-	17.3	8.7×10^{-2}	-	-

55 Industrial Utility

Fe-Cr alloys of improved workability and high-temperature strength having excellent acid resistance and/or oxidation resistance are provided. Such Fe-Cr alloys may be suitably utilized in such applications as

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automobile exhaust pipes.

[C] Inventions of category C

5 The present invention is hereinafter described in further detail by referring to the Examples.

(Example 1) Alloys 1 to 10 of the invention and Comparative alloys 1 to 7 corresponding to Claims 9 and 10

10 Alloys having the chemical compositions shown in Table 1 were prepared by melting and casting the materials in a 10 kg vacuum melting furnace, and the alloys were hot rolled into hot rolled plates of 4 mm thick. The plates were further subjected to recrystallization annealing, descaling, and cold rolling to produce cold rolled plates of 0.7 mm thick. Finally, the plates were subjected to a recrystallization annealing to produce annealed cold rolled plates.

The resulting alloy plates were subjected to the tests as described below.

15

(Workability)

Alloys 1 and 6 of the invention and Comparative alloys 1 and 6 were subjected to a tensile test according to JIS Z-2241 to evaluate for their elongation. The plates were also subjected to a bend test by 20 tightly folding to 180° in C direction after cold rolling to 50%. After the bend test, the plates were examined for cracks, and evaluated in accordance with the following criteria:

- O: no crack,
- Δ: minute cracks, and
- X: large cracks.

25 The results are shown in Table 2.

As apparent from the results, no cracks were observed upon complete bending in C direction after 50% cold rolling when the C, N, O, P and S were reduced to a total content of 100 ppm or less, while the alloy plates having a total content of C, N, O, P and S in excess of 100 ppm exhibited cracks, indicating their reduced workability. Similarly, when the elongation is compared among the alloy plates having equivalent 30 Cr and Mo contents, the elongation is inferior to the extent of about 7 to 8% in the alloy plates having the total content of C, N, O, P and S in excess of 100 ppm.

(Pitting resistance and acid resistance)

35 Test pieces of Comparative alloy 2, and Alloys 1 and 7 of the invention were ground finished with Emery #500. The test pieces were then evaluated for their pitting resistance by immersing in an aqueous solution of (2% FeCl₃ + 1/20 HCl) at 30°C for 4 hours, and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The test pieces were also evaluated for their acid resistance by immersing in a 0.1 % by weight aqueous solution of HCl for 4 hours and measuring their 40 weight loss caused by the corrosion to thereby calculate their corrosion rate. The results are shown in Table 2.

The above procedure was repeated to prepare test samples of Comparative alloy 5, and Alloys 10 and 6 of the invention. The test samples were then evaluated for their pitting resistance by immersing in an aqueous solution of (5% FeCl₃ + 1/20 N HCl) at 30°C for 4 hours, and measuring their weight loss caused 45 by the corrosion to thereby calculate their corrosion rate. The test samples were also evaluated for their acid resistance by immersing in a 0.3 % by weight aqueous solution of HCl for 4 hours and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The results are shown in Table 2.

The above procedure was repeated to prepare test samples of Comparative alloy 4, and Alloys 4 and 5 50 of the invention. The test samples were then evaluated for their pitting resistance by immersing in an aqueous solution of (5% FeCl₃ + 1/20 N HCl) at 30°C for 4 hours, and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The test samples were also evaluated for their acid resistance by immersing in a 0.3 % by weight aqueous solution of HCl for 4 hours and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The results are shown in Table 55 2.

The above procedure was repeated to prepare test samples of Comparative alloy 3, and Alloys 2 and 8 of the invention. The test samples were then evaluated for their pitting resistance by immersing in an aqueous solution of (5% FeCl₃ + 1/20 N HCl) at 80°C for 4 hours, and measuring their weight loss caused

by the corrosion to thereby calculate their corrosion rate. The test samples were also evaluated for their acid resistance by immersing in a 5 % by weight aqueous solution of HCl for 4 hours and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The results are shown in Table 2.

5 The above procedure was repeated to prepare test samples of Comparative alloy 7, and Alloys 3 and 9 of the invention. The test samples were then evaluated for their pitting resistance by immersing in an aqueous solution of (10% FeCl₃ + 1/20 N HCl) at 80 °C for 4 hours, and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The test samples were also evaluated for their acid resistance by immersing in a 5 % by weight aqueous solution of HCl for 4 hours and measuring
10 their weight loss caused by the corrosion to thereby calculate their corrosion rate. The results are shown in Table 2.

The above results reveal that the pitting resistance may be markedly improved by the inclusion of Mo in an amount within the range of the present invention, and that the acid resistance may be additionally improved by the inclusion of the Ni, Co and Cu in an amount within the range of the present invention.

15 (Example 2) Alloys 11 to 25 of the invention and Comparative alloys 8 to 11 corresponding to Claim 11

Alloys having the chemical compositions shown in Table 1 were prepared in an ultra high-vacuum melting furnace of 10⁻⁷ Torr or less from an ultra high-purity electrolytic iron, an electrolytic Cr and other
20 high-purity metal materials.

The alloy materials were heated to about 1,200 °C and hot rolled into plates of about 5 mm thick, and finally, cold rolled to a thickness of 1.0 to 2.0 mm. The plates were further annealed at 500 to 1,100 °C for recrystallization and particle size adjustment.

Test samples were cut out of the thus prepared alloy materials for tensile tests at room temperature and at an elevated temperature in accordance with Japanese Industrial Standard (The tensile test at room
25 temperature was carried out in accordance with JIS 5, and the tensile test at an elevated temperature was carried out in accordance with JIS G 0567).

The alloy materials of the Table 1 prepared in an ultra high-vacuum furnace from high-purity metals were also subjected to an oxidation test wherein the alloy materials were heated in an electric furnace open
30 to atmosphere to 1,350 K for 12 hours, and cooled by air to room temperature, and measured for their weight loss after scale removal. The thus evaluated weight loss was used as an index for their oxidation resistance. The results are shown in Table 2.

The results reveal that the oxidation resistance may be significantly improved by the inclusion of either or both of Al, Si and Mn; or Ca, Mg and REM in an amount within the range of the present invention.

35 (Example 3) Alloys 26 and 27 of the invention corresponding to Claim 12

Alloys having the chemical compositions shown in Table 1 were prepared in an ultra high-vacuum melting furnace of 10⁻⁷ Torr or less from an ultra high-purity electrolytic iron, an electrolytic Cr and other
40 high-purity metal materials.

The alloy materials were heated to about 1,200 °C and hot rolled into plates of about 5 mm thick, and finally, cold rolled to a thickness of 1.0 to 2.0 mm. The plates were further annealed at 500 to 1,100 °C for recrystallization and particle size adjustment.

The test samples were then evaluated for their acid resistance and oxidation resistance. The results
45 clearly reveal that the test samples of the present invention have excellent properties.

The test results are shown in Table 2.

(Increase in elongation and decrease in proof stress)

50 The test samples obtained in all of the above-described examples were evaluated for their increase in elongation and decrease in proof stress (yield strength). The increase in elongation (%) and the decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm.

The tensile properties used for such calculation are:

55 Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

Table 1 (2)

Alloys of invention											
	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements
13	7	30	18	10	9	15.4	1.0	3.850	1.030	1.600	
14	13	10	16	15	19	30.4	2.5	0.013	0.036	0.003	
15	9	15	16	18	15	29.6	2.5	0.030	0.020	0.050	
16	15	9	21	10	15	30.1	2.3	3.510	0.960	1.580	
17	11	19	33	11	8	16.0	1.1	0.003	0.002	0.010	REM:0.0015
18	7	30	10	10	13	15.5	1.3	0.010	0.008	0.007	Ca:0.0004,Mg:0.0004
19	9	16	23	15	9	16.3	0.9	0.006	0.015	0.005	Ca:0.011,Mg:0.009, REM:0.026
20	9	13	16	21	15	30.3	1.9	0.003	0.006	0.010	Ca:0.0005
21	13	9	31	11	10	28.6	1.9	0.002	0.013	0.006	Ca:0.0011,Mg:0.0006
22	8	15	18	18	13	31.0	2.0	0.012	0.012	0.005	Ca:0.009,Mg:0.006, REM:0.036
23	10	29	15	10	25	16.0	0.8	0.080	0.120	0.030	Ca:0.0013,Mg:0.0009, REM:0.004
24	11	31	16	10	9	15.8	1.1	0.100	0.060	0.090	Ca:0.0026,REM:0.0010

Unit: wt%, *: ppm.

 $\alpha = \text{C+N+O+S+P}$, $\beta = \text{Ni+Co+2Cu}$, $\gamma = 3\text{Al}+2\text{Si}+\text{Mn}$, $\delta = 4\text{Ca}+4\text{Mg}+\text{REM}$

Table 1 (3)

Alloys of invention	Alloys of invention														
	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements	α^*	β	γ	δ
	β	γ	δ												
23	15	9	23	10	15	29.6	2.3	0.090	0.080	0.150	Ca:0.0014, Mg:0.0013	72	—	0.570	0.0108
26	10	26	31	10	11	15.3	1.3	0.090	0.060	0.070	Ca:0.0016, Mg:0.0010, RbA:0.005, Ni:0.13, Co:0.12, Cu:0.04	88	0.33	0.460	0.0154
27	9	30	26	15	9	31.2	1.8	0.110	0.090	0.130	Mg:0.0020, RbA:0.011, Co:0.12, Cu:0.12	89	0.36	0.640	0.0190

Unit: wt%, *: ppm

α =C+N+O+S+P, β =Ni+Co+2Cu, γ =3Al+2Si+Mn, δ =4Ca+4Mg+REM

Table 1 (4)

	Comparative alloys											δ
	C*	N*	O*	P*	S*	Cr	Mo	Al	Si	Mn	Other elements	
1	32	40	35	10	15	5.1	2.70	0.006	0.010	0.008		132
2	10	10	20	12	15	5.1	0.09	0.005	0.008	0.009		67
3	30	10	30	12	5	29.4	0.35	0.005	0.012	0.023		87
4	5	3	7	5	8	18.5	0.02	0.008	0.006	0.005	Ni:0.006	26
5	25	10	22	15	10	15.6	0.08	0.010	0.007	0.008		88
6	46	30	25	185	15	15.5	1.60	0.005	0.017	0.022	Cu:0.54	301
7	13	36	25	33	10	42.6	0.02	0.002	0.010	0.009		117
8	36	39	31	20	25	15.9	1.10	0.010	0.010	0.006		151
9	38	29	45	20	15	30.2	2.30	0.012	0.005	0.013		147
10	9	23	31	15	9	16.3	0.28	0.013	0.008	0.006		87
11	13	9	26	11	18	31.0	0.30	0.005	0.012	0.008		77

Unit: wt%, *: ppm

 $\alpha = \text{C+N+O+S+P}$, $\beta = \text{Ni+Co+2Cu}$, $\gamma = 3\text{Al}+2\text{Si+Mn}$, $\delta = 4\text{Ca}+4\text{Mg+REM}$

Table 2 (1)

	Increase in elongation stress (%)	Decrease in proof stress (N/mm ²)	Elongation (%)	Bend- ing to 180°	Pitting resistance-weight loss, g/m ² ·hr				Oxidation resistance weight loss, g/m ² ·hr			Weight loss in oxidation g/cm ² ·12hr
					2%FeCl ₃ + 1/20 N·HCl 30°C	5%FeCl ₃ + 1/20 N·HCl 30°C	5%FeCl ₃ + 1/20 N·HCl 80°C	10%FeCl ₃ + 1/20 N·HCl 80°C	0.1% HCl	0.3% HCl	5% HCl	
1	+ 5.8	- 95	41	○	5.9	-	-	-	6.60	-	-	-
2	+ 6.2	- 90	-	-	-	-	≤ 0.01	-	-	-	3.1	-
3	+ 8.5	- 111	-	-	-	-	-	≤ 0.01	-	-	1.0	-
4	+ 8.9	- 130	-	-	-	5.0	-	-	-	5.9	-	-
5	+ 10.9	- 148	-	-	-	5.2	-	-	-	4.0	-	-
6	+ 5.8	- 89	37	○	-	4.9	-	-	-	4.7	-	-
7	+ 9.1	- 121	-	-	5.6	-	-	-	2.90	-	-	-
8	+ 6.5	- 105	-	-	-	-	≤ 0.01	-	-	-	1.2	-
9	+ 9.3	- 124	-	-	-	-	-	≤ 0.01	-	-	0.06	-
10	+ 7.3	- 111	-	-	-	4.9	-	-	-	6.0	-	-

Alloys of invention

Table 2 (2)

	Increase in elongation (%)	Decrease in proof stress (N/mm ²)	Bend- ing (°)	Pitting resistance-weight loss, g/m ² ·hr				Oxidation resistance weight loss, g/m ² ·hr			Weight loss in oxidation g/cm ² ·12hr
				2.96FeCl ₃ + 1/20 N·HCl 30°C	5.96FeCl ₃ + 1/20 N·HCl 30°C	5.96FeCl ₃ + 1/20 N·HCl 80°C	10% FeCl ₃ + 1/20 N·HCl 80°C	0.1wt% HCl	0.3wt% HCl	5wt% HCl	
11	+ 8.1	-119	-	-	4.9	-	-	-	-	-	1.3×10^{-4}
12	+ 6.0	- 88	-	-	4.8	-	-	-	-	-	1.1×10^{-4}
13	+ 7.0	-100	-	-	3.8	-	-	-	-	-	$<1.0 \times 10^{-4}$
14	+ 7.2	-100	-	-	-	≤ 0.01	-	-	-	-	$<1.0 \times 10^{-4}$
15	+ 8.0	- 89	-	-	-	≤ 0.01	-	-	-	-	$<1.0 \times 10^{-4}$
16	+ 7.8	-103	-	-	-	≤ 0.01	-	-	-	-	$<1.0 \times 10^{-4}$
17	+ 6.5	- 90	-	-	4.8	-	-	-	-	-	1.8×10^{-4}
18	+ 8.0	-100	-	-	4.9	-	-	-	-	-	$<1.0 \times 10^{-4}$
19	+ 6.9	- 95	-	-	5.2	-	-	-	-	-	$<1.0 \times 10^{-4}$
20	+ 8.0	-100	-	-	-	≤ 0.01	-	-	-	-	$<1.0 \times 10^{-4}$

Alloys of invention

Table 2 (3)

	Increase in elongation stress (N/mm ²)	Decrease in elongation stress (N/mm ²)	Elongation (N)	Non-elongation (N)	Pitting resistance-weight loss, g/m ² ·hr				Oxidation resistance weight loss, g/m ² ·hr			Weight loss in oxidation g/cm ² ·12hr
					296FeCl ₃ + 1/20 N·HCl 30°C	596FeCl ₃ + 1/20 N·HCl 30°C	596FeCl ₃ + 1/20 N·HCl 80°C	10% FeCl ₃ + 1/20 N·HCl 80°C	0.1wt% HCl	0.3wt% HCl	5wt% HCl	
21	+ 7.6	- 87	-	-	-	-	≤ 0.01	-	-	-	-	< 1.0 × 10 ⁻⁴
22	+ 7.5	- 90	-	-	-	-	≤ 0.01	-	-	-	-	< 1.0 × 10 ⁻⁴
23	+ 6.8	- 89	-	-	-	4.6	-	-	-	-	-	< 1.0 × 10 ⁻⁴
24	+ 6.1	- 88	-	-	-	4.9	-	-	-	-	-	< 1.0 × 10 ⁻⁴
25	+ 8.0	- 99	-	-	-	-	≤ 0.01	-	-	-	-	< 1.0 × 10 ⁻⁴
26	+ 5.9	- 90	-	-	-	5.0	-	-	-	4.0	-	< 1.0 × 10 ⁻⁴
27	+ 7.5	- 88	-	-	-	-	≤ 0.01	-	-	-	1.1	< 1.0 × 10 ⁻⁴

Alloys of Invention

Table 2 (4)

	Increase in elongation (%)	Decrease in proof stress (N/mm ²)	Bend- ing to 180°	Pitting resistance-Weight loss, g/m ² ·hr				Oxidation resistance Weight loss, g/m ² ·hr			Weight loss in oxidation g/cm ² ·12hr
				2.96FeCl ₃ + 1/20 N·HCl 30°C	5.96FeCl ₃ + 1/20 N·HCl 30°C	5.96FeCl ₃ + 1/20 N·HCl 80°C	10% FeCl ₃ + 1/20 N·HCl 80°C	0.1wt% HCl	0.3wt% HCl	5wt% HCl	
1	+2.3	-46	3.4	△	-	-	-	-	-	-	-
2	+7.5	-89	-	-	126	-	-	680	-	-	-
3	+5.9	-90	-	-	-	0.9	-	-	-	3.5	-
4	+11.0	-128	-	-	8.0	-	-	-	70	-	-
5	+5.6	-95	-	-	10.7	-	-	-	86	-	-
6	+1.3	-26	2.9	×	-	-	-	-	-	-	-
7	+3.0	-36	-	-	-	-	1.8	-	-	4.9	-
8	+2.8	-46	-	-	8.3	-	-	-	-	-	1.3 × 10 ⁻¹
9	+2.9	-39	-	-	-	1.5	-	-	-	-	8.9 × 10 ⁻¹
10	+5.8	-83	-	-	9.8	-	-	-	-	-	1.6 × 10 ⁻¹
11	+7.0	-90	-	-	-	1.2	-	-	-	-	7.5 × 10 ⁻¹

Comparative alloys

55 Industrial Utility

The alloys according to the present invention have excellent acid resistance and/or oxidation resistance in addition to improved workability and pitting resistance, and therefore, may be suitably utilized in such

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applications as automobile exhaust pipes.

[D] Inventions of category D

5 The present invention is hereinafter described in further detail by referring to the Examples.

(Example 1)

10 Alloys having the chemical compositions shown in Table 1 were prepared by melting and casting the materials in a 10 kg vacuum melting furnace, and the alloys were hot rolled into hot rolled plates of 4 mm thick. The plates were further subjected to recrystallization annealing, descaling, and cold rolling to produce cold rolled plates of 0.7 mm thick. Finally, the plates were subjected to a recrystallization annealing to produce annealed cold rolled plates.

The resulting alloy plates were subjected to the tests as described below.

15

(Workability)

Alloys 1 and 2 of the invention and Comparative alloys 1 and 2 were subjected to a tensile test according to JIS Z-2241 to evaluate for their elongation. The plates were also subjected to a bend test by tightly folding to 180° in C direction after cold rolling to 50%. After the bend test, the plates were examined for cracks, and evaluated in accordance with the following criteria:

O: no crack,
Δ: minute cracks, and
X: large cracks.

25 The results are shown in Table 2.

As apparent from the results, no cracks were observed upon complete bending in C direction after 50% cold rolling when the C, N, O, P and S were reduced to a total content of 100 ppm or less, while the alloy plates having a total content of C, N, O, P and S in excess of 100 ppm exhibited cracks, indicating their reduced workability. Similarly, when the elongation is compared among the alloy plates having equivalent Cr and Mo contents, the elongation is inferior to the extent of about 5 to 6% in the alloy plates having the total content of C, N, O, P and S in excess of 100 ppm.

30

(Pitting resistance and intergranular corrosion resistance)

35 Test pieces were ground finished with Emery #500. The test pieces were then evaluated for their pitting resistance by immersing in aqueous solutions of $\text{FeCl}_3 + \text{HCl}$ shown in Table 2 for 4 hours, and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The test pieces were also evaluated for their intergranular corrosion resistance by subjecting the test pieces to TIG welding (bead on), sulfuric acid-copper sulfate test according to JIS G-0572, and weld zone bend test ($r = 2t$, bending to 180°), and examining the test pieces for the presence or the absence of cracks.

40

O: no crack,
Δ: minute cracks, and
X: large cracks.

The results are shown in Table 2.

45

(Intergranular corrosion resistance and acid resistance)

Test samples were prepared by repeating the above-described procedure, and the test samples were evaluated for their intergranular corrosion resistance by the same procedure as described above. The test samples were also evaluated for their acid resistance by immersing in aqueous HCl solutions shown in Table 2 for 24 hours and measuring their weight loss caused by the corrosion to thereby calculate their corrosion rate. The results are shown in Table 2.

50

(Oxidation resistance)

55

The oxidation test was carried out by heat treating the test samples in air at 1350°K for 12 hours, and descaling the heat treated samples. The samples were then weighed to determine their weight loss.

The results are shown in Table 2.

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(Increase in elongation and decrease in proof stress)

The resulting test samples were evaluated for their increase in elongation and decrease in proof stress (yield strength). The increase in elongation (%) and the decrease in proof stress (yield strength) (N/mm²) indicate difference in respective tensile properties from the alloy having the (C + N + O + S + P) of 500 ppm.

The tensile properties used for such calculation are:

Fe - 18% Cr; C + N + O + S + P = 500 ppm

elongation: 30%

proof stress: 330 N/mm²

Fe - 30% Cr; C + N + O + S + P = 500 ppm

elongation: 25%

proof stress: 450 N/mm²

The above results reveal that the pitting resistance may be markedly improved by the inclusion of Mo in an amount within the range of the present invention, and that the intergranular corrosion resistance in the weld zone may be improved by the inclusion of Ti, Nb, V, Ta, W, Zr, and/or B in an adequate amount. Furthermore, the above results reveal that the acid resistance may be significantly improved by the inclusion of the Ni, Co and/or Cu in an adequate amount. Still further, the above results reveal that the oxidation resistance may be significantly improved by the inclusion in an adequate amount of at least one member selected from Si, Mn and Al; and/or at least one member selected from Ca, Mg and REM.

Table 1 (1)

	Alloys of invention										Mn	Ti, Nb, Zr, V, Ta, W, B
	* C	* N	* O	* P	* S	Cr	Mo	Al	Si			
1	15	10	20	15	12	5.4	0.8	0.007	0.015		0.016	Ti 0.02, Nb 0.06 V 0.005
2	5	12	30	8	25	11.4	1.7	0.010	0.007		0.006	Ti 0.015, Ta 0.006 W 0.003
3	20	5	5	4	5	17.9	0.6	0.006	0.008		0.007	Zr 0.01, Nb 0.04
4	35	15	18	10	15	26.5	3.2	0.004	0.008		0.015	Nb 0.26, B 0.0005
5	8	7	15	15	25	26.5	3.2	0.012	0.004		0.003	B 0.0018, V 0.13
6	25	10	10	5	5	45.3	0.8	0.005	0.009		0.006	Nb 0.04, Zr 0.01
7	25	15	30	18	5	45.3	0.7	0.006	0.010		0.007	Ti 0.80
8	9	10	21	10	9	17.8	0.8	0.07	0.03		0.05	Nb 0.09
9	16	16	9	15	11	17.6	0.7	3.25	1.00		0.96	Ti 0.08, B 0.0008

Unit: wt%, *: ppm

 $\alpha = \text{C} + \text{N} + \text{O} + \text{P} + \text{S}$, $\beta = \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B}$, $\gamma = \text{Ni} + \text{Co} + 20\text{u}$, $\delta = 3\text{Al} + 2\text{Si} + \text{Mn}$, $\epsilon = 4\text{Ca} + 4\text{Mg} + \text{REM}$

Table 1 (2)

	Other elements	α^*	β	γ	δ	ϵ
1	—	72	0.085	—	—	—
2	—	80	0.024	—	—	—
3	—	39	0.05	—	—	—
4	—	93	0.285	—	—	—
5	Ni 0.06, Co 0.10	70	0.38	0.16	—	—
6	Cu 0.005	55	0.05	0.01	—	—
7	Ni 0.21	93	0.80	0.21	—	—
8	—	59	0.09	—	0.32	—
9	—	67	0.12	—	12.71	—

Unit: wt%, *: ppm

 $\alpha = \text{C+N+O+P+S}$, $\beta = \text{Ti+Nb+Zr+V+Ta+W+50B}$,
 $\gamma = \text{Ni+Co+2Cu}$, $\delta = 3\text{Al}+2\text{Si}+\text{Mn}$, $\epsilon = 4\text{Ca}+4\text{Mg}+\text{REM}$

Table 1 (3)

	Alloys of invention										Mn	Ti, Nb, Zr, V, Ta, W, B
	* C	* N	* O	* P	* S	Cr	Mo	Al	Si			
10	8	30	18	13	15	26.8	3.3	0.04	0.08		0.04	Nb 0.05, Ti 0.02 Zr 0.03
11	22	15	6	10	13	26.5	3.4	2.80	1.30		1.21	Ti 0.03, Nb 0.06
12	10	18	18	9	12	17.8	0.7	0.006	0.003		0.005	Zr 0.02, Ta 0.02 V 0.02
13	8	18	20	18	10	17.8	0.8	0.010	0.011		0.005	Nb 0.01, W 0.03
14	10	13	25	10	10	27.0	2.9	0.005	0.002		0.003	Ta 0.061
15	9	9	30	15	10	27.1	3.3	0.008	0.006		0.009	V 0.028
16	11	21	26	20	11	17.6	0.8	0.03	0.02		0.05	W 0.039
17	9	18	29	10	10	17.8	0.8	0.09	0.06		0.11	Ti 0.110
18	7	10	11	10	10	29.3	0.7	0.06	0.05		0.13	Nb 0.003, Ti 0.002 V 0.011, B 0.0008

Unit: wt%, *: ppm
 $\alpha = \text{C} + \text{N} + \text{O} + \text{P} + \text{S}$, $\beta = \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B}$,
 $\gamma = \text{Ni} + \text{Co} + 2\text{Cu}$, $\delta = 3\text{Al} + 2\text{Si} + \text{Mn}$, $\epsilon = 4\text{Ca} + 4\text{Mg} + \text{REM}$

Table 1 (4)

Alloys of invention						
	Other elements	α *	β	γ	δ	ε
10	—	84	0.10	—	0.32	—
11	—	66	0.09	—	12.21	—
12	REM 0.002	67	0.06	—	0.029	0.002
13	Ca 0.009 REM 0.011	74	0.04	—	0.057	0.047
14	Mg 0.0009	68	0.061	—	0.024	0.0036
15	Mg 0.010 REM 0.023	73	0.028	—	0.045	0.063
16	Ca 0.0011	89	0.039	—	0.20	0.0044
17	Mg 0.0010 Ni 0.10, Cu 0.03	76	0.110	0.16	0.50	0.0040
18	Ca 0.0008 Mg 0.0006 REM 0.002, Ni 0.05 Co 0.05, Cu 0.03	48	0.056	0.16	0.41	0.0076

Unit: wt%, *: ppm
 $\alpha = \text{C} + \text{N} + \text{O} + \text{P} + \text{S}$, $\beta = \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + \text{50B}$,
 $\gamma = \text{Ni} + \text{Co} + \text{2Cu}$, $\delta = \text{3Al} + \text{2Si} + \text{Mn}$, $\varepsilon = \text{4Ca} + \text{4Mg} + \text{REM}$

Table 1 (5)

	Comparative alloys										Ti, Nb, Zr, V, Ta, W, B
	* C	* N	* O	* P	* S	Cr	Mo	Al	Si	Mn	
1	16	25	35	20	38	5.5	0.7	0.008	0.015	0.014	Ti 0.04, Nb 0.06 V 0.03
2	51	40	25	14	15	11.5	1.6	0.008	0.016	0.017	Ti 0.018, Ta 0.007 W 0.004
3	25	15	10	10	5	18.0	0.03	0.005	0.007	0.006	Zr 0.03, Nb 0.10
4	15	10	12	8	15	17.8	0.7	0.010	0.007	0.005	V 0.003, Ti 0.005
5	13	9	21	10	13	27.7	0.08	0.009	0.013	0.009	Nb 0.05
6	11	19	10	11	12	46.3	0.05	0.012	0.010	0.011	Nb 0.02, Zr 0.03

Unit: wt%, *: ppm

 $\alpha = C + N + O + P + S$, $\beta = Ti + Nb + Zr + V + Ta + W + B$, $\gamma = Ni + Co + 2Cu$, $\delta = 3Al + 2Si + Mn$, $\epsilon = 4Ca + Mg + RE$

Table 1 (6)

	Other elements	α^*	β	γ	δ	ϵ
1	—	134	0.13	—	0.068	—
2	Ni 0.03, Co 0.05	271	0.029	0.08	0.073	—
3	—	65	0.13	—	0.035	—
4	—	60	0.008	—	0.049	—
5	—	66	0.05	—	0.062	—
6	—	63	0.05	—	0.067	—

Unit: wt%, *: ppm

 $\alpha = \text{C+N+O+P+S}$, $\beta = \text{Ti+Nb+Zr+V+Ta+W+50B}$,
 $\gamma = \text{Ni+Co+2Cu}$, $\delta = 3\text{Al}+2\text{Si+Mn}$, $\epsilon = 4\text{Ca}+4\text{Mg+REN}$

Table 2 (1)

	Increase in elon- gation (%)	Decrease in yield strength (N/mm ²)	Elon- gation (%)	Bend- ing to 180°	Pitting resistance-weight loss, g/m ² ·hr			
					2%FeCl ₃ + 1/20N · HCl 30°C	5%FeCl ₃ + 1/20N · HCl 30°C	5%FeCl ₃ + 1/20N · HCl 80°C	10%FeCl ₃ + 1/20N · HCl 80°C
Alloys of invention	1 + 8.0	- 103	41	○	6.0	-	-	-
	2 + 6.5	- 90	37	○	11	-	-	-
	3 + 10.0	- 121	-	-	-	4.0	-	-
	4 + 5.9	- 90	-	-	-	-	≤ 0.01	-
	5 + 7.0	- 100	-	-	-	-	≤ 0.01	-
	6 + 10.3	- 111	-	-	-	-	-	≤ 0.01
	7 + 6.5	- 90	-	-	-	-	-	≤ 0.01
	8 + 8.1	- 119	-	-	-	3.9	-	-
	9 + 7.0	- 108	-	-	-	3.7	-	-

Table 2 (2)

		Oxidation resistance weight loss, g/m ² ·hr			Weight loss in oxidation g/m ² ·12hr	Bending after sulfuric acid-copper sulfate test
		0.1wt% HCl	0.3wt% HCl	5wt% HCl		
Alloys of invention	1	—	—	—	—	○
	2	—	—	—	—	○
	3	—	—	—	8.0×10^{-4}	○
	4	—	—	3.1	2.6×10^{-4}	○
	5	—	—	1.0	—	○
	6	—	—	1.2	—	○
	7	—	—	<0.1	—	○
	8	—	—	—	$\leq 1.0 \times 10^{-4}$	○
	9	—	—	—	$\leq 1.0 \times 10^{-4}$	○

Table 2 (3)

	Increase in elongation (%)	Decrease in yield strength (N/mm ²)	Elongation (%)	Bend- ing to 180°	Pitting resistance-weight loss, g/m ² ·hr			
					2%FeCl ₃ + 1/20N · HCl 30°C	5%FeCl ₃ + 1/20N · HCl 30°C	5%FeCl ₃ + 1/20N · HCl 80°C	10%FeCl ₃ + 1/20N · HCl 80°C
Alloys of invention	10 + 6.3	- 100	-	-	-	-	≤ 0.01	-
	11 + 8.0	- 113	-	-	-	-	≤ 0.01	-
	12 + 7.9	- 108	-	-	-	4. 0	-	-
	13 + 6.9	- 100	-	-	-	4. 0	-	-
	14 + 8.9	- 110	-	-	-	-	≤ 0.01	-
	15 + 8.0	- 96	-	-	-	-	≤ 0.01	-
	16 + 6.0	- 91	-	-	-	4. 0	-	-
	17 + 7.1	- 100	-	-	-	3. 9	-	-
	18 + 10.5	- 123	-	-	-	-	≤ 0.01	-

Table 2 (4)

	Oxidation resistance weight loss, g/m ² .hr			Weight loss in oxidation g/m ² .12hr	Bending after sulfuric acid-copper sulfate test
	0.1wt% HCl	0.3wt% HCl	5wt% HCl		
10	-	-	-	$\leq 1.0 \times 10^{-4}$	○
11	-	-	-	$\leq 1.0 \times 10^{-4}$	○
12	-	-	-	$\leq 1.0 \times 10^{-4}$	○
13	-	-	-	$\leq 1.0 \times 10^{-4}$	○
14	-	-	-	$\leq 1.0 \times 10^{-4}$	○
15	-	-	-	$\leq 1.0 \times 10^{-4}$	○
16	-	-	-	$\leq 1.0 \times 10^{-4}$	○
17	-	-	-	$\leq 1.0 \times 10^{-4}$	○
18	-	-	-	$\leq 1.0 \times 10^{-4}$	○

Alloys of invention

Table 2 (5)

	Increase in elongation (%)	Decrease in yield strength (N/mm ²)	Elongation (%)	Bending to 100°	Pitting resistance-Weight loss, g/m ² .hr			
					28%FeCl ₃ + 1/20N · HCl 30°C	5%FeCl ₃ + 1/20N · HCl 30°C	5%FeCl ₃ + 1/20N · HCl 80°C	10%FeCl ₃ + 1/20N · HCl 80°C
1	+ 3.0	- 49	36	△	101	-	-	-
2	+ 1.6	- 28	31	×	63	-	-	-
3	+ 7.1	- 96	-	-	-	10.2	-	-
4	+ 8.3	- 110	-	-	-	4.3	-	-
5	+ 7.9	- 105	-	-	-	-	0.8	-
6	+ 9.3	- 110	-	-	-	-	-	1.3

Comparative alloys

Table 2 (6)

	Comparative alloys	Oxidation resistance			Weight loss in oxidation g/m ² · 12hr	Bending after sulfuric acid-copper sulfate test
		Weight loss, g/m ² · hr				
		0.1wt% HCl	0.3wt% HCl	5wt% HCl		
1		—	—	—	○	
2		—	—	—	×	
3		—	—	—	○	
4		—	—	—	△	
5		—	—	—	○	
6		—	—	—	○	

Industrial Utility

The Fe-Cr alloys according to the present invention containing C, N, O, P and S in a total amount of 100 ppm or less and a predetermined amount of Mo and at least one member selected from Ti, Nb, Zr, V, Ta, W and B have excellent workability as well as significantly improved pitting resistance and weld zone corrosion resistance (intergranular corrosion resistance).

The Fe-Cr alloys further comprising a predetermined amount of at least one member selected from Ni, Cu and Co has a significantly improved acid resistance in addition to the above-mentioned properties.

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Further addition of at least one member selected from Si, Mn and Al and/or at least one member selected from Ca, Mg and REM results in an improved oxidation resistance. The resulting alloy plates are useful in a wide varieties of applications.

5 Claims

1. An Fe-Cr alloy having an excellent workability characterized in that the alloy comprises 3 to 60% by weight of Cr; and 100 ppm or less in total content of C, N, O, P and S; the balance being Fe and inevitable impurities.
2. An Fe-Cr alloy having excellent workability and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and at least one member selected from Ni, Co and Cu at a content that meets the following relation (1):
$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1);$$
the balance being Fe and inevitable impurities.
3. An Fe-Cr alloy having excellent workability and oxidation resistance characterized in that the alloy comprises 3 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and at least one member selected from Si, Mn and Al at a content that meets the following relation (2):
$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (2),$$
and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):
$$0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (3);$$
the balance being Fe and inevitable impurities.
4. An Fe-Cr alloy having excellent workability, acid resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; at least one member selected from Ni, Co and Cu at a content that meets the following relation (1):
$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (1);$$
and at least one member selected from Si, Mn and Al at a content that meets the following relation (2):
$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (2),$$
and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):
$$0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (3);$$
the balance being Fe and inevitable impurities.
5. An Fe-Cr alloy having excellent workability and high-temperature strength characterized in that the alloy comprises 3 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):
$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt \%} \quad (1);$$
the balance being Fe and inevitable impurities.
6. An Fe-Cr alloy having excellent workability, high-temperature strength, and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O,

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P and S; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt\%} \quad (1);$$

and at least one member selected from Ni, Co and Cu at a content that, meets the following relation (2):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (2);$$

the balance being Fe and inevitable impurities.

7. An Fe-Cr alloy having excellent workability, high-temperature strength, and oxidation resistance characterized in that the alloy comprises 3 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt\%} \quad (1);$$

and at least one member selected from Al, Si and Mn at a content that meets the following relation (3):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (3),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (4);$$

the balance being Fe and inevitable impurities.

8. An Fe-Cr alloy having excellent workability, high-temperature strength, acid resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 6 \text{ wt\%} \quad (1);$$

at least one member selected from Ni, Co and Cu at a content that meets the following relation (2):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (2);$$

and at least one member selected from Al, Si and Mn at a content that meets the following relation (3):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (3),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (4);$$

the balance being Fe and inevitable impurities.

9. An Fe-Cr alloy having excellent workability and pitting resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; and 0.5 to 20% by weight of Mo; the balance being Fe and inevitable impurities.

10. An Fe-Cr alloy having excellent workability, pitting resistance, and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5

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to 20% by weight of Mo; and at least one member selected from Ni, Cu and Co at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (1);$$

the balance being Fe and inevitable impurities.

11. An Fe-Cr alloy having excellent workability, pitting resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; and at least one member selected from Al, Si and Mn at a content that meets the following relation (2):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (2),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (3);$$

the balance being Fe and inevitable impurities.

12. An Fe-Cr alloy having excellent workability, pitting resistance, acid resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ni, Cu and Co at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (1);$$

and at least one member selected from Al, Si and Mn at a content that meets the following relation (2):

$$0.1 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (2),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (3):

$$0.001 \text{ wt\%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt\%} \quad (3);$$

the balance being Fe and inevitable impurities.

13. An Fe-Cr alloy having excellent workability, pitting resistance, and weld corrosion resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; and at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt\%} \quad (1);$$

the balance being Fe and inevitable impurities.

14. An Fe-Cr alloy having excellent workability, pitting resistance, weld corrosion resistance, and acid resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt\%} \quad (1);$$

and at least one member selected from Ni, Cu and Co at a content that meets the following relation (2):

$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%} \quad (2);$$

the balance being Fe and inevitable impurities.

- 5 15. An Fe-Cr alloy having excellent workability, pitting resistance, weld corrosion resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

10
$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt \%} \quad (1);$$

and at least one member selected from Si, Mn and Al at a content that meets the following relation (3):

$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (3),$$

- 15 and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

$$0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (4);$$

20 the balance being Fe and inevitable impurities.

16. An Fe-Cr alloy having excellent workability, pitting resistance, weld corrosion resistance, acid resistance, and oxidation resistance characterized in that the alloy comprises 5 to 60% by weight of Cr; 100 ppm or less in total content of C, N, O, P and S; 0.5 to 20% by weight of Mo; at least one member selected from Ti, Nb, Zr, V, Ta, W and B at a content that meets the following relation (1):

25
$$0.01 \text{ wt \%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 50\text{B} \leq 1.0 \text{ wt \%} \quad (1);$$

at least one member selected from Ni, Cu and Co at a content that meets the following relation (2):

30
$$0.01 \text{ wt \%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt \%} \quad (2);$$

and at least one member selected from Si, Mn and Al at a content that meets the following relation (3):

35
$$0.1 \text{ wt \%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt \%} \quad (3),$$

and/or at least one member selected from Ca, Mg and rare earth metals (REM) at a content that meets the following relation (4):

40
$$0.001 \text{ wt \%} \leq 4\text{Ca} + 4\text{Mg} + \text{REM} \leq 0.2 \text{ wt \%} \quad (4);$$

the balance being Fe and inevitable impurities.

45

50

55

FIG. 1

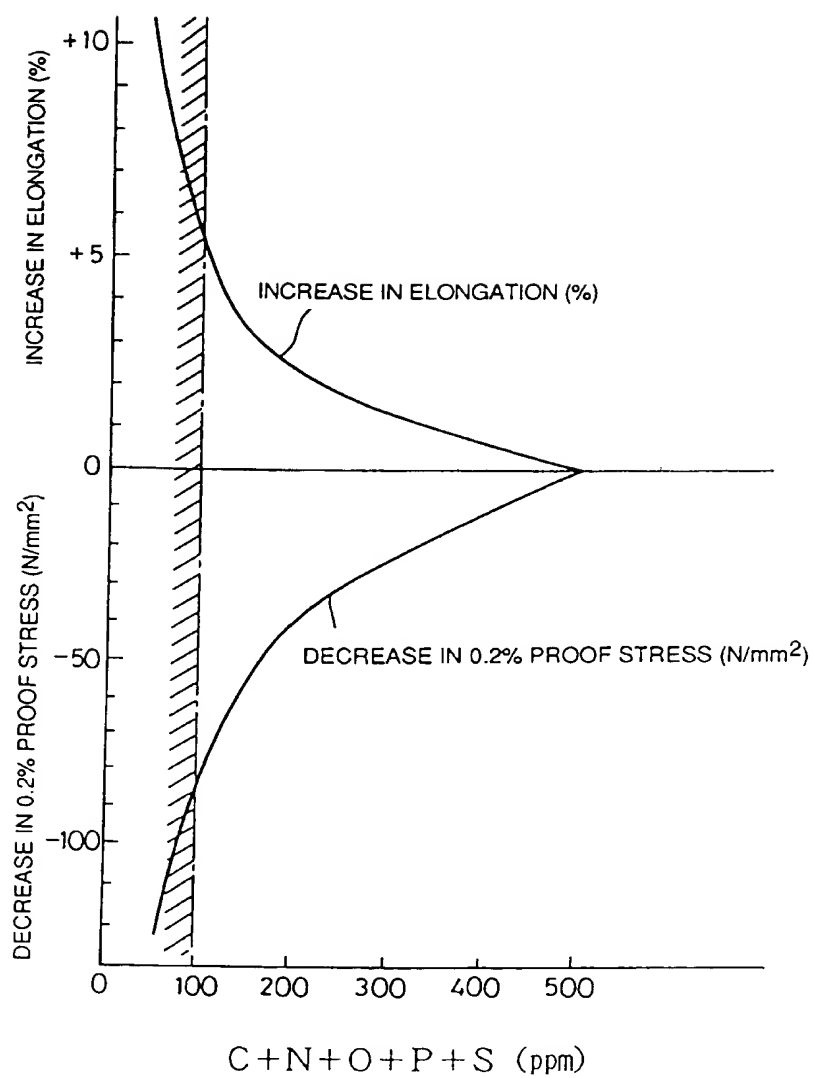


FIG. 2

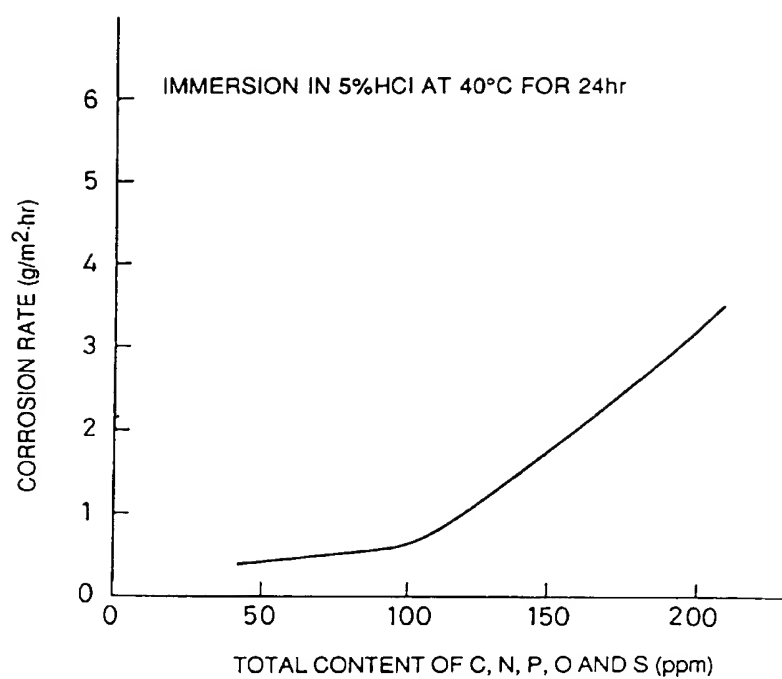


FIG. 3

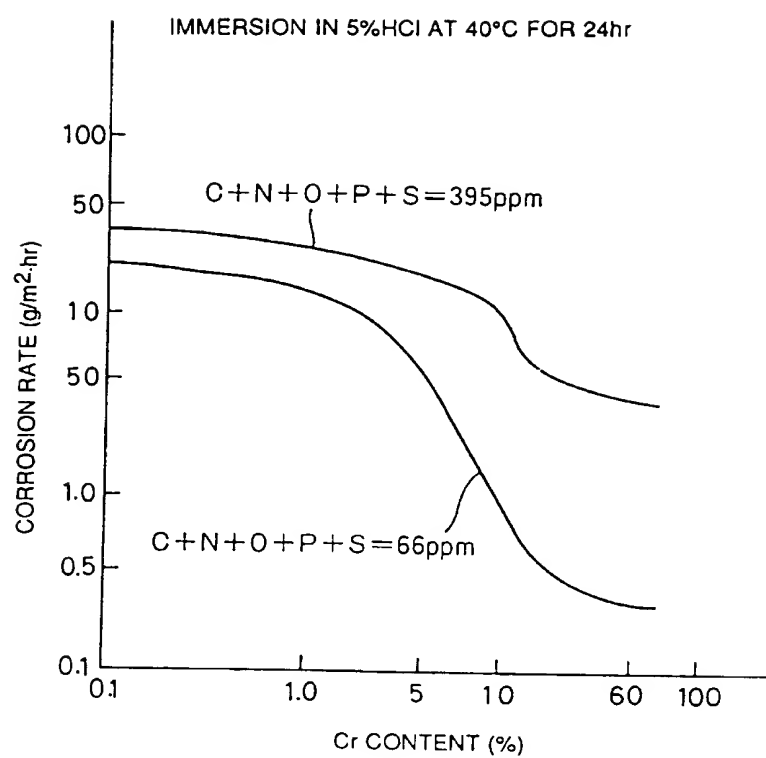


FIG. 4

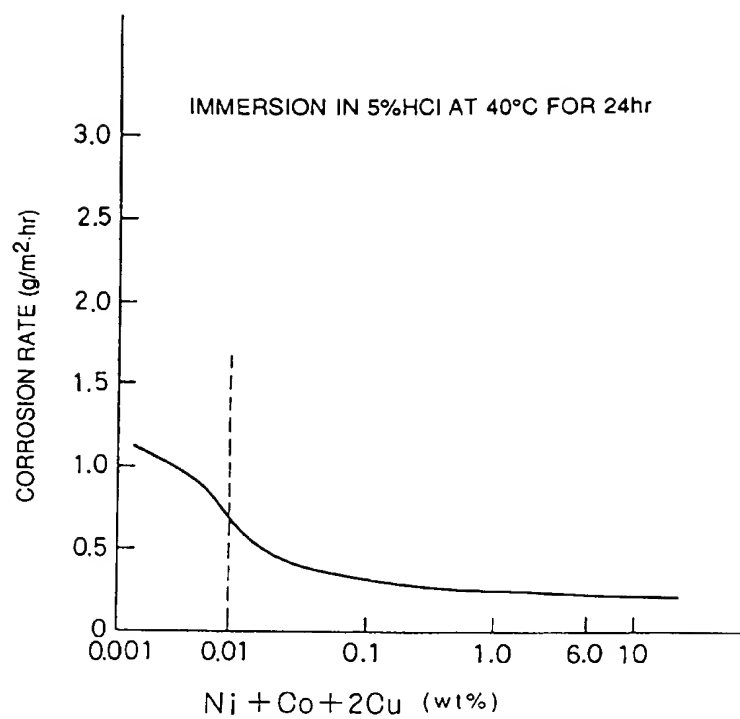


FIG. 5

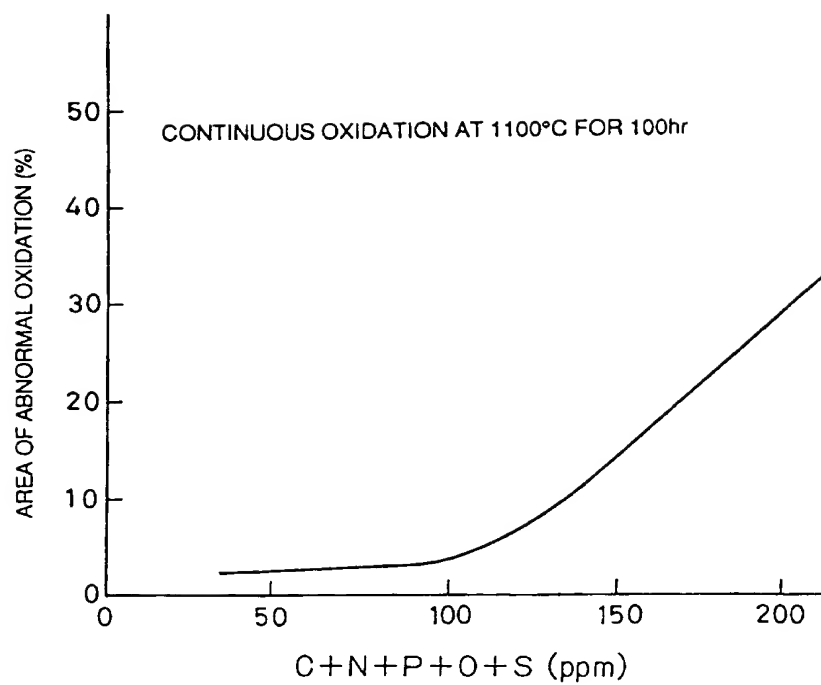


FIG. 6

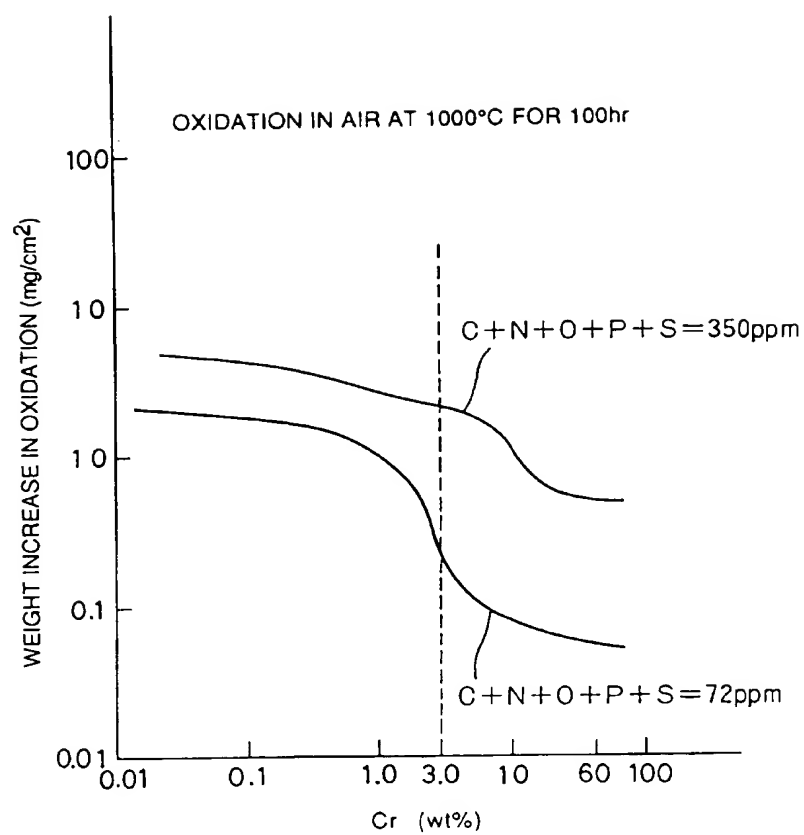


FIG. 7

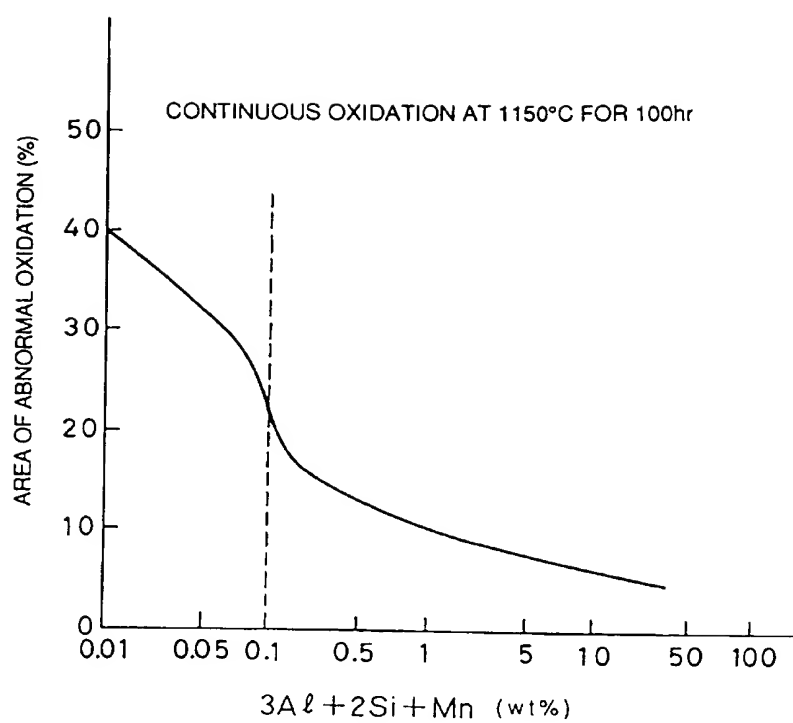


FIG. 8

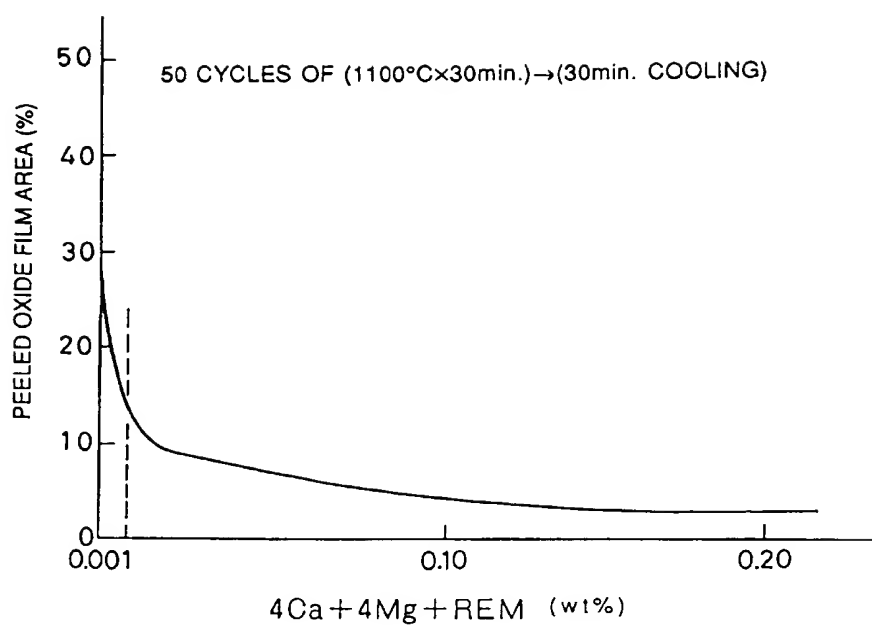


FIG. 9

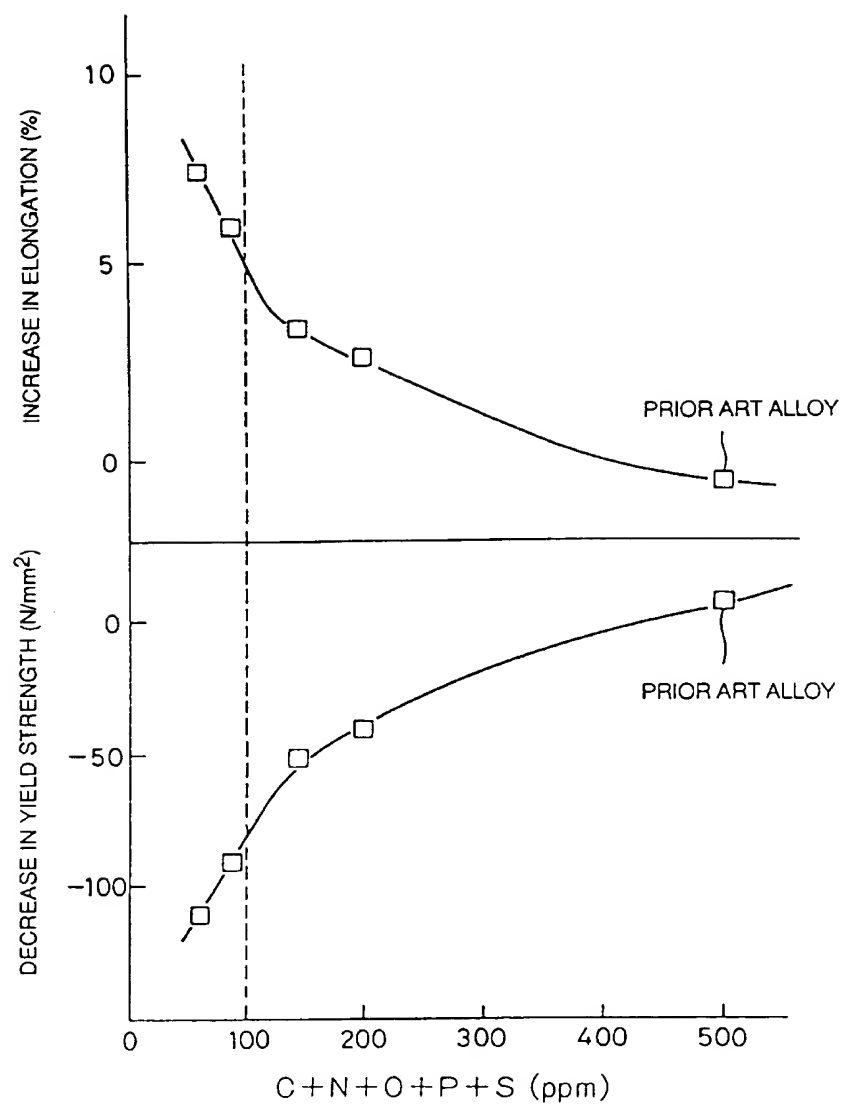


FIG. 10

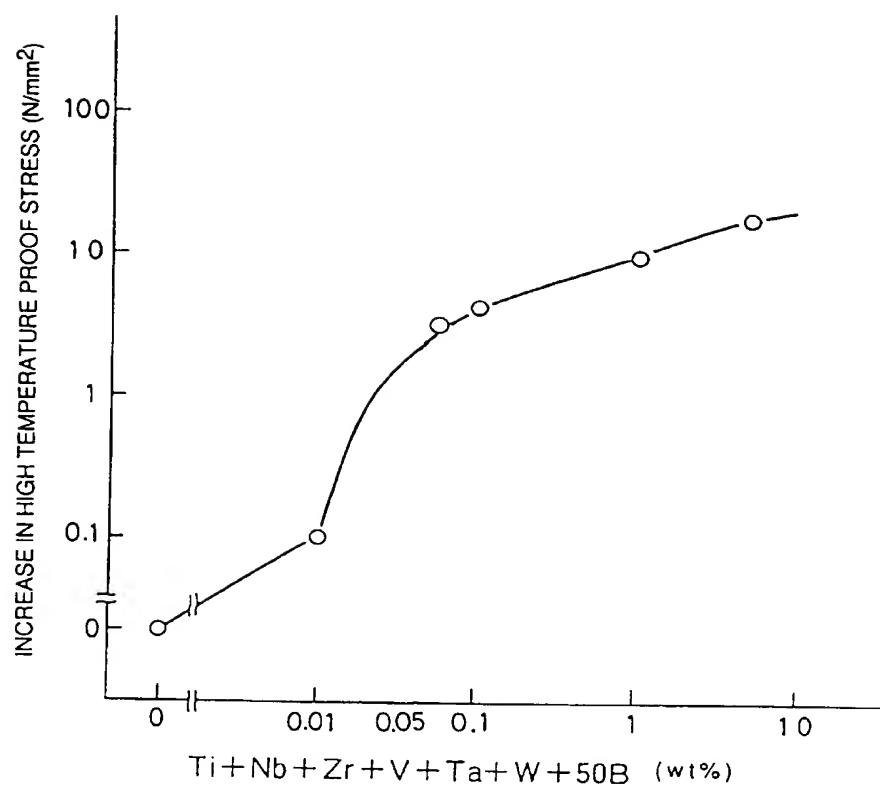


FIG. 11

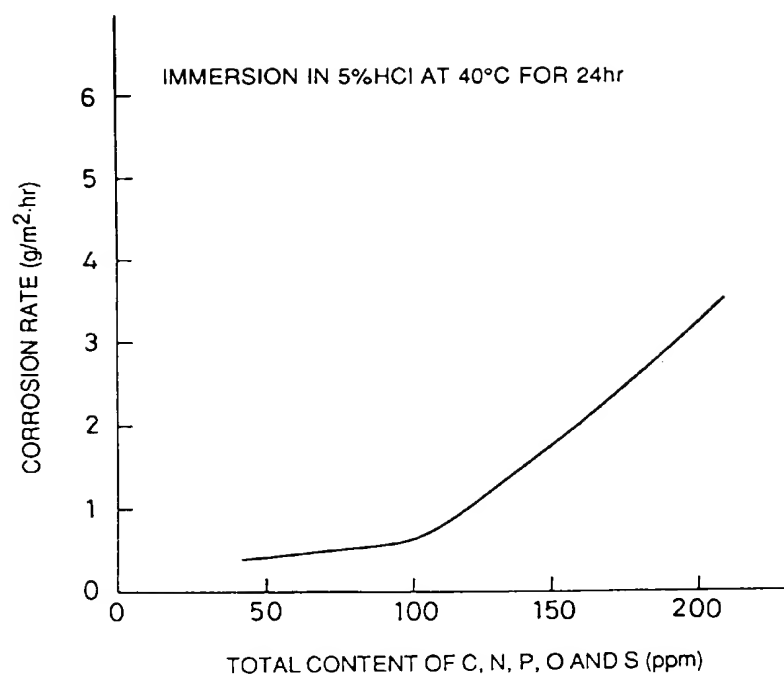


FIG. 12

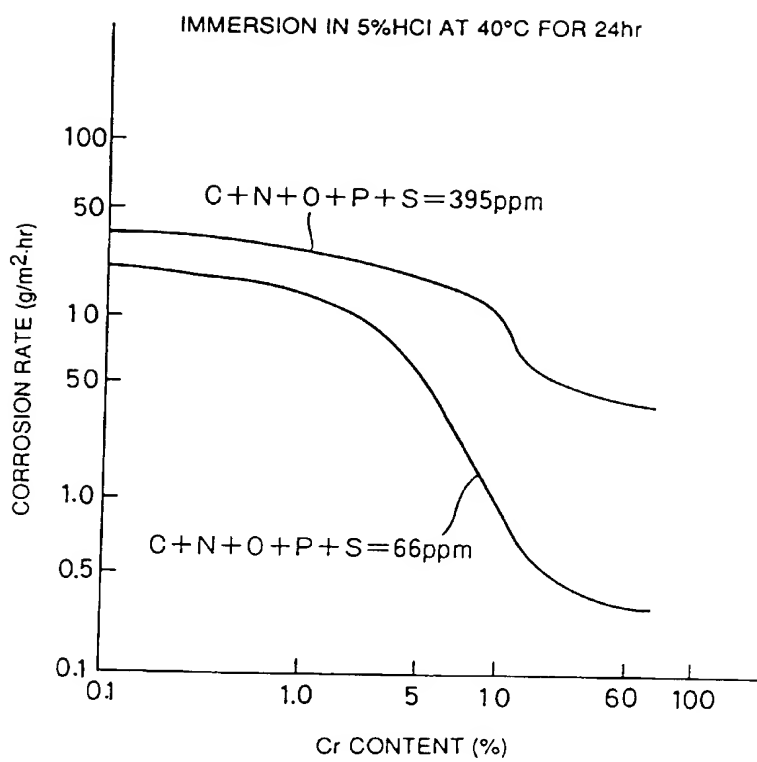


FIG. 13

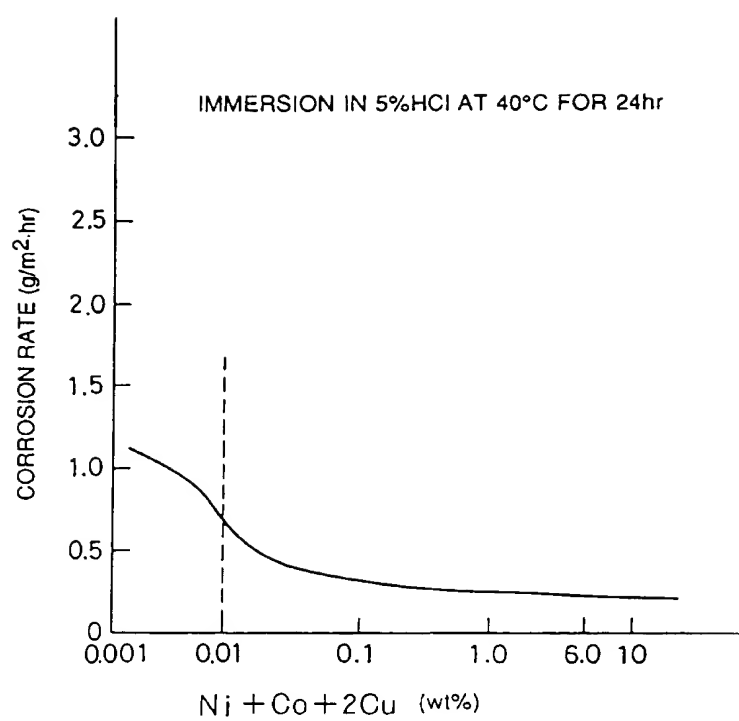


FIG. 14

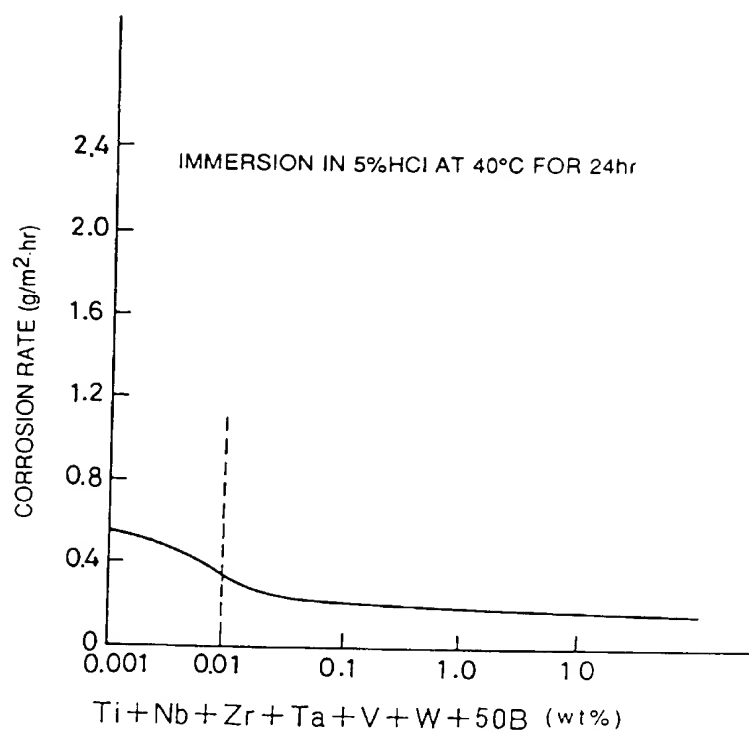


FIG. 15

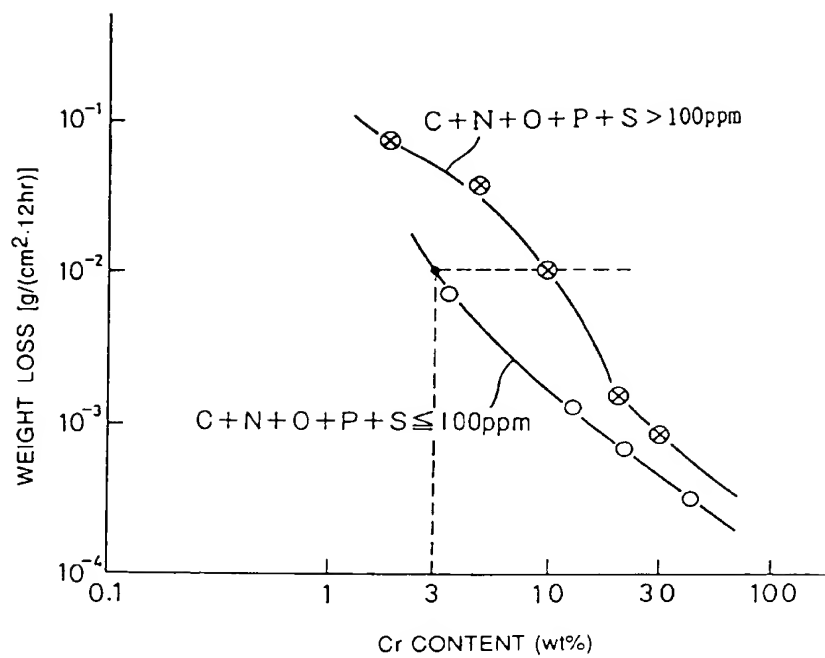


FIG. 16

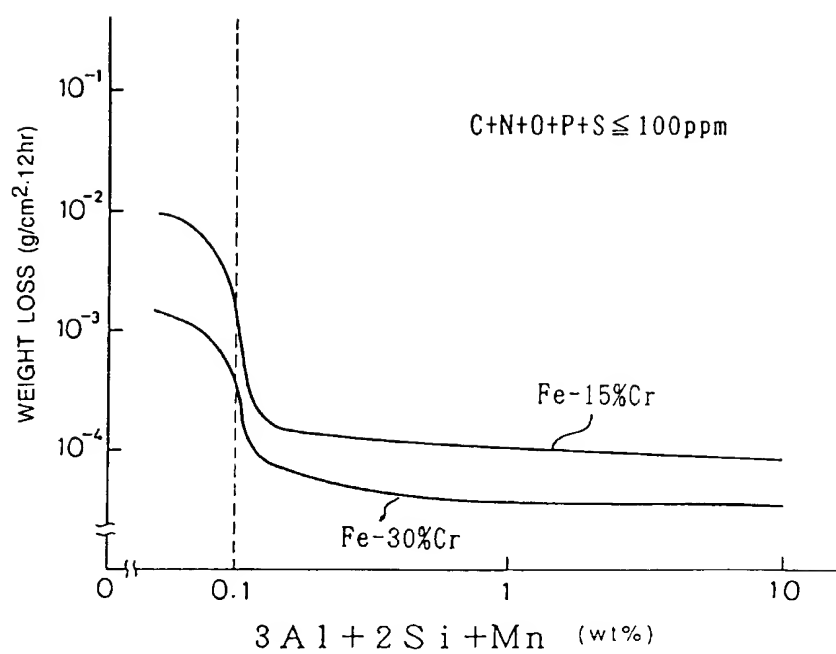


FIG. 17

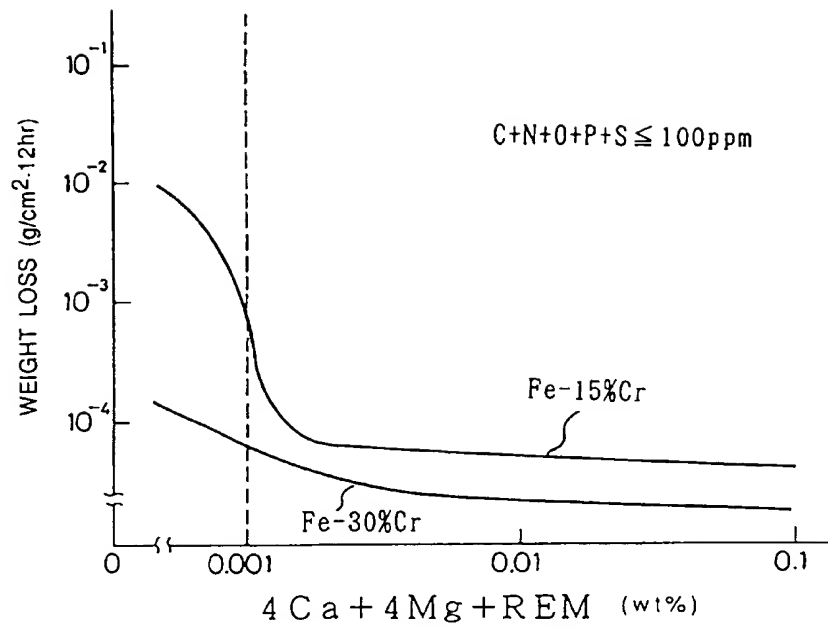


FIG. 18

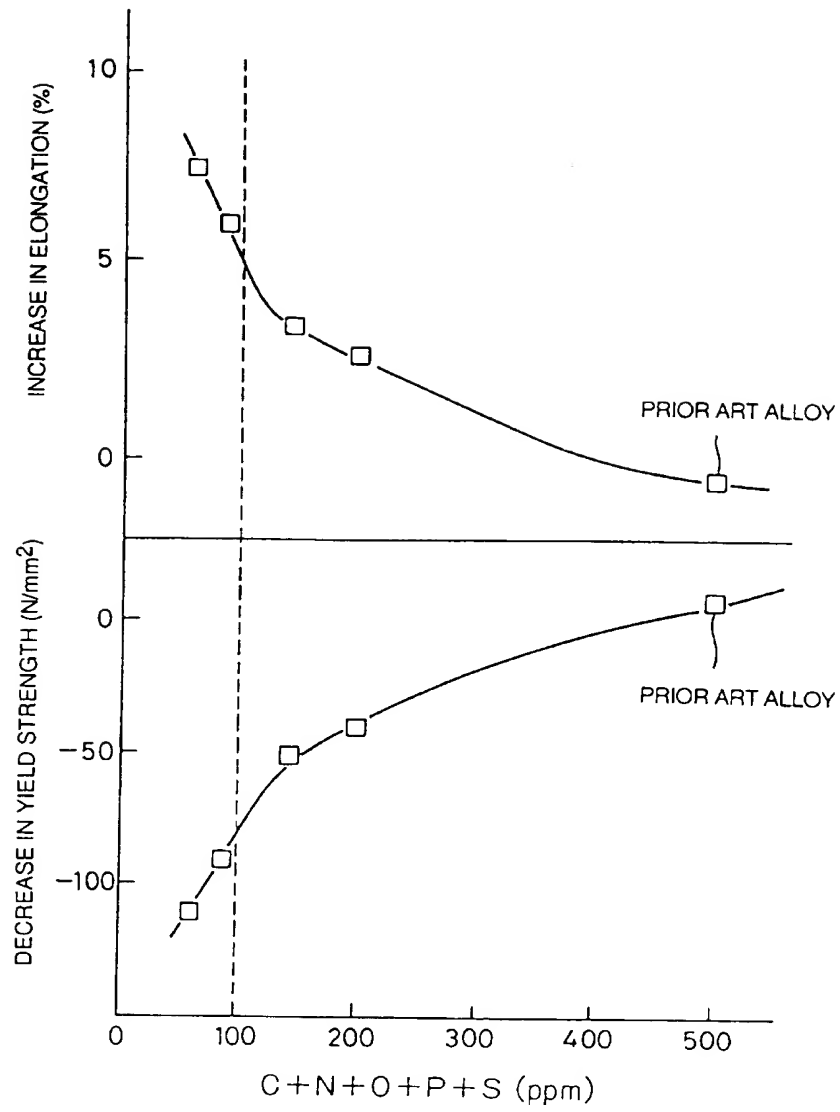


FIG. 19

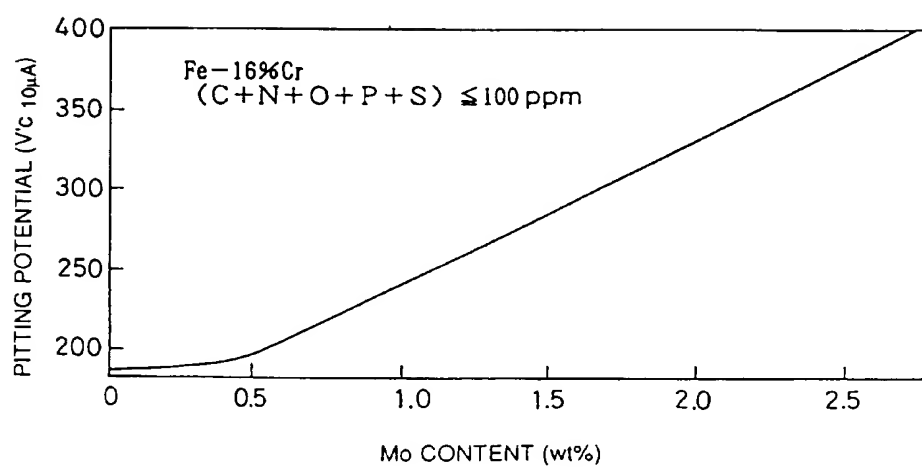


FIG. 20

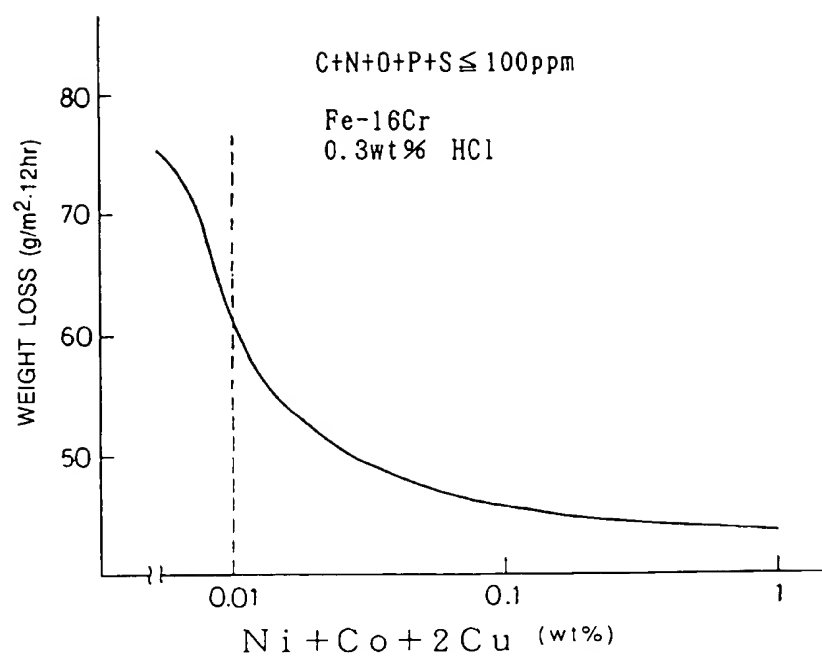


FIG. 21

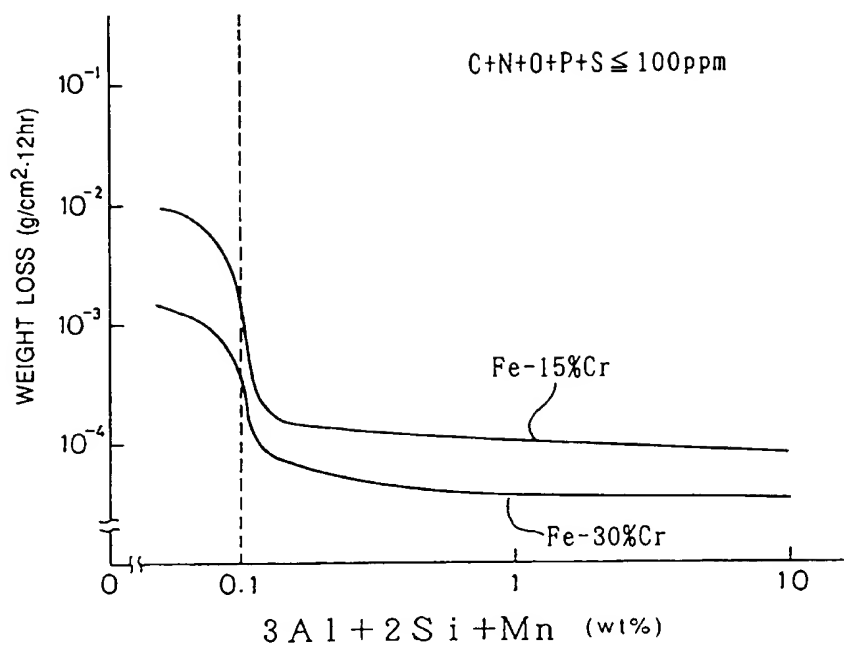


FIG. 22

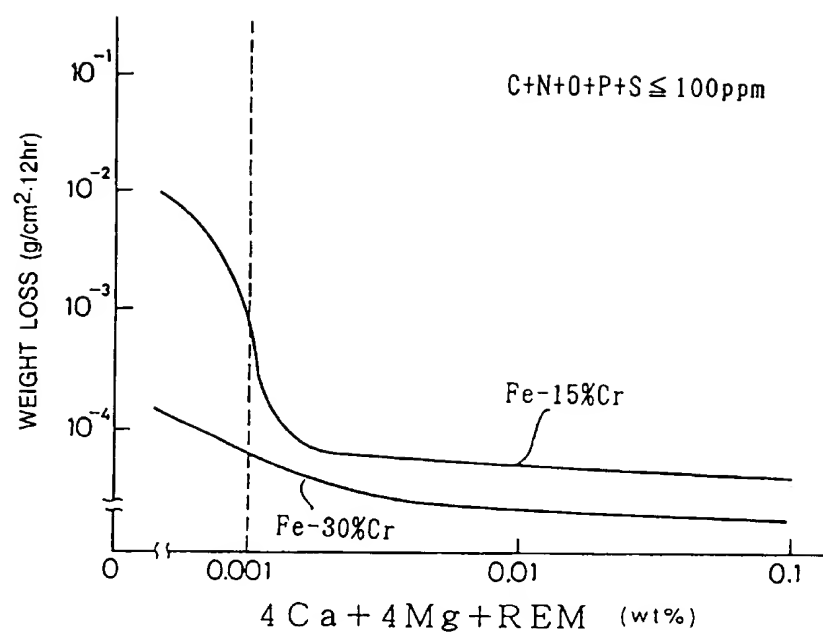


FIG. 23

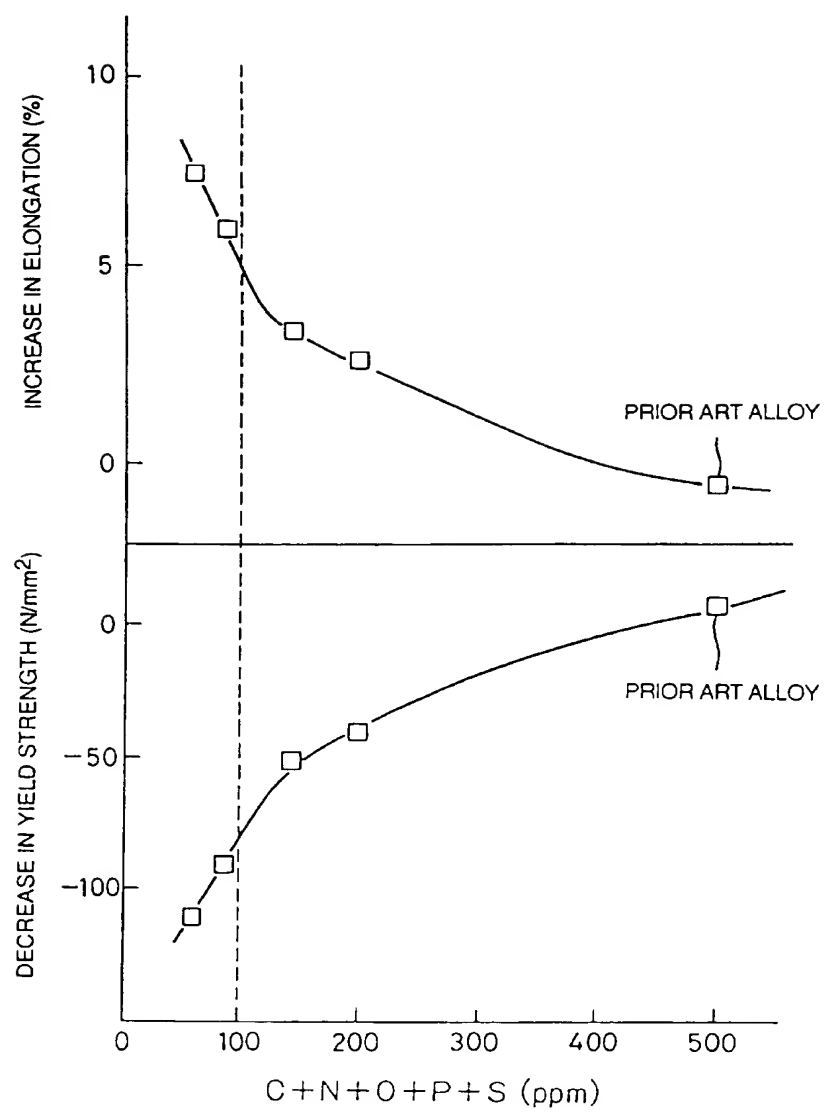


FIG. 24

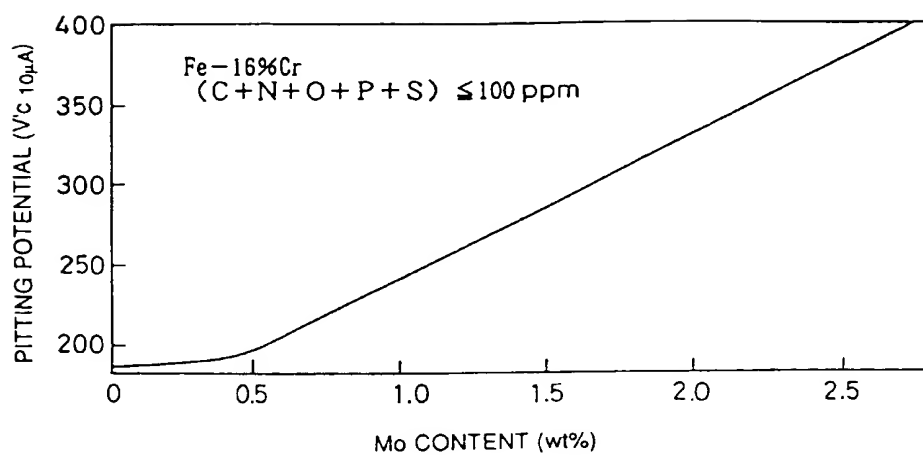


FIG. 25

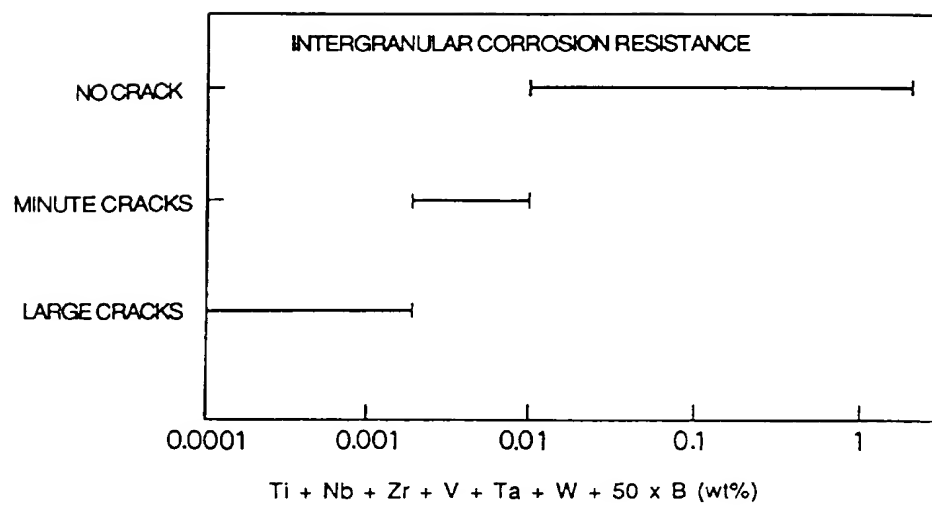


FIG. 26

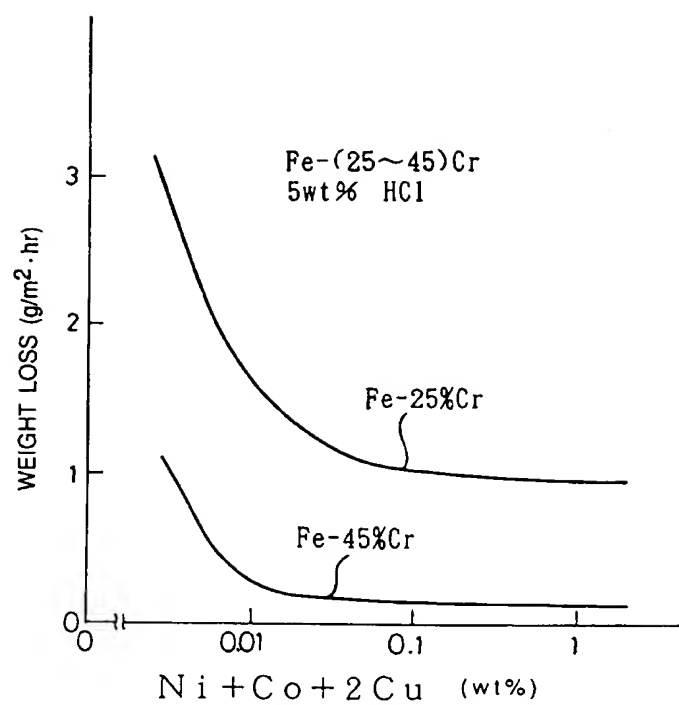


FIG. 27

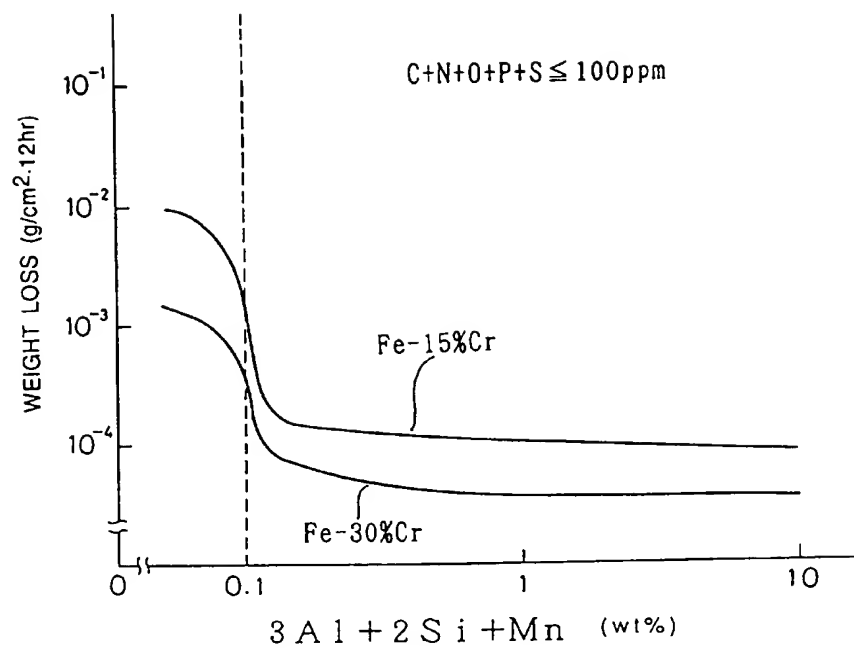
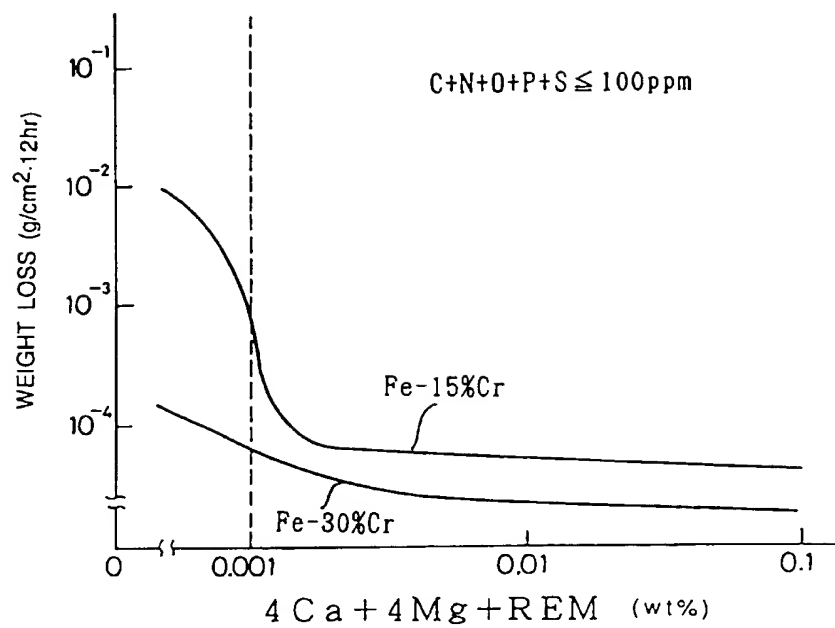


FIG. 28



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00580

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl ⁵ C22C38/18, 38/54		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl ⁵ C22C38/00-38/54		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, B2, 63-58904 (Nisshin Steel Co., Ltd.), November 17, 1988 (17. 11. 88), Page 1 (Family: none)	7 1, 3, 5
X Y	JP, A, 1-287253 (Nisshin Steel Co., Ltd.), November 17, 1989 (17. 11. 89), Page 1 (Family: none)	3, 7 1, 5
X Y	JP, B2, 59-38300 (Sumitomo Metal Industries, Ltd.), September 14, 1984 (14. 09. 84), Line 26, column 26 to line 13, column 2 & US, A, 4360381	8, 15, 16 1-7, 9-14
	JP, B2, 2-14419 (Nippon Steel Corp.),	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search July 23, 1993 (23. 07. 93)		Date of mailing of the international search report August 10, 1993 (10. 08. 93)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00580

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	April 9, 1990 (09. 04. 90), Line 28, columns 1 to 4 (Family: none)	4, 6-8, 11-16 1-3, 5, 9, 10
X Y	JP, B2, 61-23259 (Nippon Steel Corp.), June 5, 1986 (05. 06. 86), Page 1 (Family: none)	8, 12, 16 1-7, 9-11, 13-15
X Y	JP, A, 62-199721 (Nisshin Steel Co., Ltd.), September 3, 1987 (03. 09. 87), Line 8, upper right column, pages 1 to 2 (Family: none)	8, 12, 16 1-7, 9-11, 13-15
X Y	JP, A, 1-172524 (Nisshin Steel Co., Ltd.), July 7, 1989 (07. 07. 89), Line 8, lower left column, pages 1 to 2 (Family: none)	12, 16 1-11, 13-15